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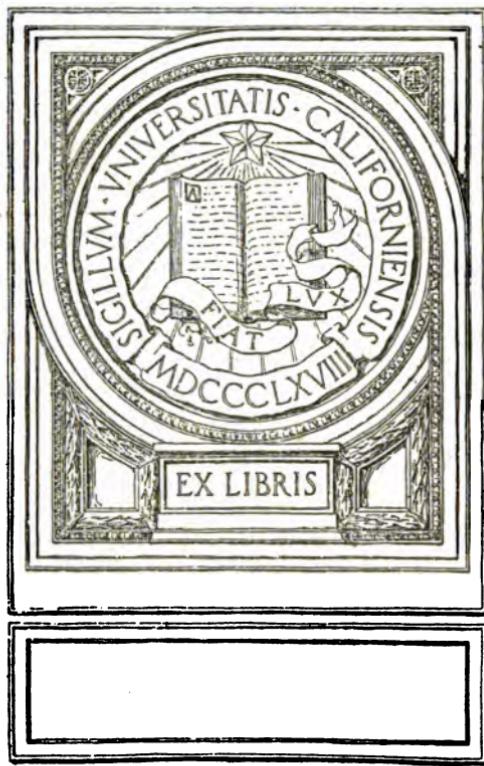
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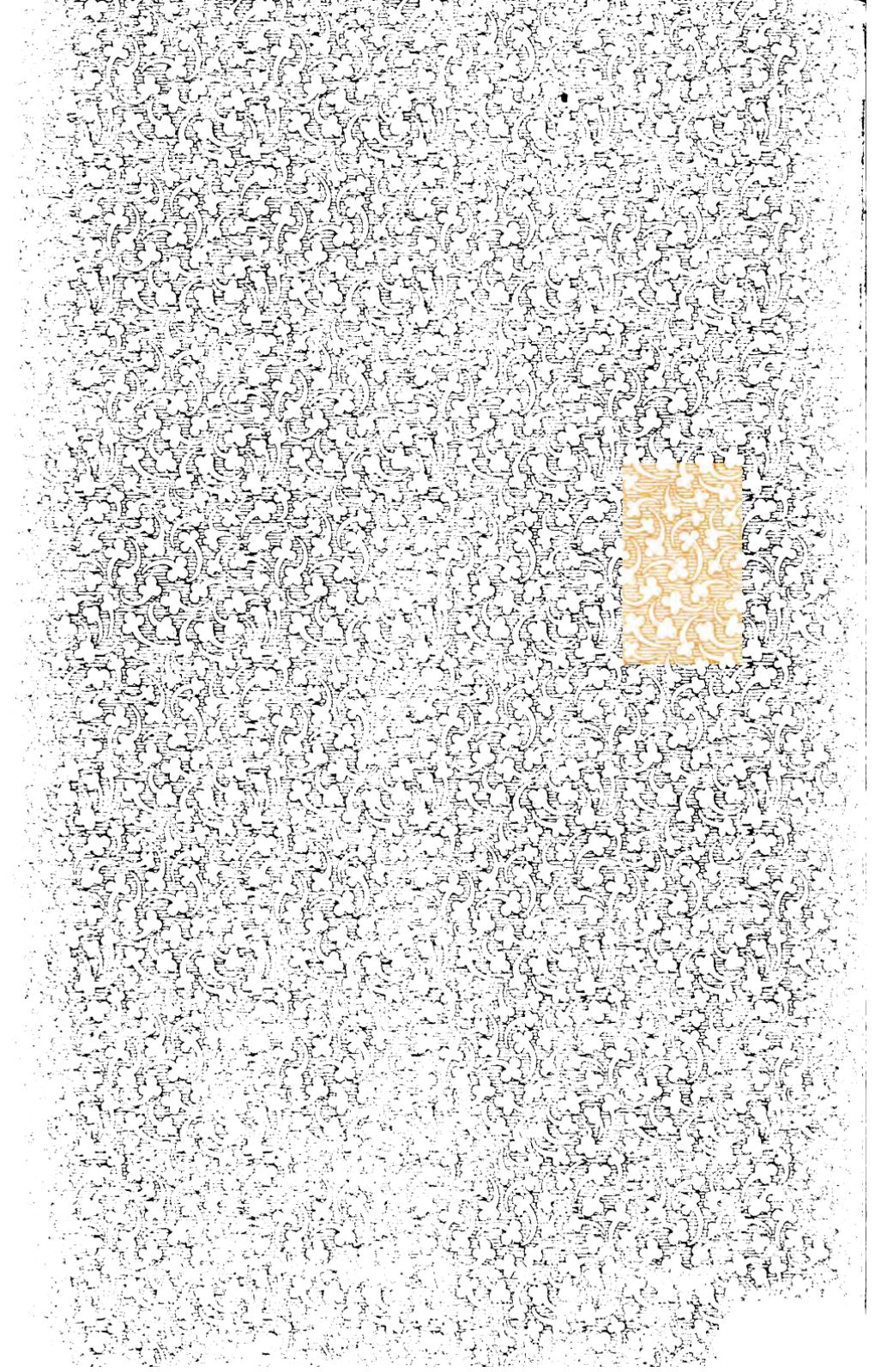
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THE CHEMISTRY OF THE RADIO-ELEMENTS

BY

FREDERICK SODDY, F.R.S.

LATELY LECTURER IN PHYSICAL CHEMISTRY AND RADIOACTIVITY
IN THE UNIVERSITY OF GLASGOW: PROFESSOR OF
CHEMISTRY, UNIVERSITY OF ABERDEEN

Author

PART I

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PREFACE TO NEW EDITION OF PART I

THE Chemistry of the Radio-Elements was first published as a single volume in 1911. Early in 1913 the important generalisation was made which connects the chemical nature of the radio-elements with the sequence of changes in which they result, and which has given rise to the theory of isotopic elements, and thrown a fresh light on the Periodic Law. These discoveries formed the subject of a new volume, published at the end of 1913, as Part II of the Chemistry of the Radio-Elements, the original volume thus becoming Part I.

In 1914, a new edition of Part I being called for, the present volume was written. The whole subject can now be presented much more clearly and completely than in 1911, and in consequence Part I has had to be largely rewritten from the new point of view. But whilst the general mode of presentation has been much modified, the ground already covered in detail in Part II has been, as far as possible, avoided in the present volume, which concerns itself rather with the practical consequences than with the theoretical significance of the new generalisations.

In addition, much new matter has been added, especially in connection with the α -rays and recent electro- and colloid-chemical researches on the radio-elements. Some of the topics but briefly dealt with before have been considerably amplified, and many new members of the disintegration series,

unknown in 1911, have had to be included. There is reason to hope that something approaching completeness has now been attained with regard to these numerous and involved successive products, and though much remains to be done, it is unlikely that many more will be discovered.

FREDERICK SODDY.

October 1914.

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THE CHEMISTRY OF THE RADIO-ELEMENTS

PART I

GENERAL DESCRIPTION OF RADIO- ACTIVITY

RADIOACTIVITY has introduced into the science of chemistry a new conception. The radioactive elements are radioactive because they are in progress of spontaneous change. The chemistry of the radio-elements is concerned largely with the nature of the products of these changes, their isolation and separate identification.

The property of radioactivity was discovered by M. Henri Becquerel¹ in 1896 for compounds of the element uranium, which he found to be spontaneously emitting new kinds of radiation, very much allied to the X-rays in their general nature. Thus the new radiations pass to varying extent through all matter, quite independently of whether it is opaque or transparent to light. The new radiations, in addition to the properties possessed by light of acting on a photographic plate and of causing certain substances, like the platinocyanides, to fluoresce, resemble the X-rays also in "ionising" the air and other gases, rendering them, for the time being, partial conductors of electricity, and causing them, for example, to discharge a gold leaf electroscope. The pioneer on the chemical side was Mme. Curie, who, working in conjunction with her husband, the late M. Pierre Curie, made the following fundamental generalisation.

Radioactivity is a property of the atom. It is not affected at all by the nature of the chemical combination in which the atom exists, nor by the physical conditions. Up

to the present day, in spite of numerous attempts, it has neither been found possible to destroy or diminish the radioactivity of a radio-element by any artificial process nor to cause an element which is not radioactive to become so. The radioactive process goes on at a definite rate and in a definite way which it is at present quite impossible to influence. This, of course, applies to the whole process. In many chemical and physical operations the radioactivity appears to be diminished or removed just as a candle burning in air appears to be destroyed. This is often simply accounted for by the escape during the process of radioactive gases or "emanations," as such have come to be styled. The sum total of radioactivity is not affected by any operation yet tried. In spite of the existence at one time of a vague belief (a belief which has no foundation), that all matter may be to a certain extent radioactive, just as all matter is believed to be to a certain extent magnetic, it is recognised to-day that radioactivity is an exceedingly rare property of matter. Of the eighty or more elements known in 1896, the year of the first discovery of the property, two only, uranium and thorium, are certainly radioactive in the now accepted full sense of that term. These two elements are at the end of the Periodic Table with the heaviest atoms known (238.2 and 232.4), and before them in the Table was a great gap, the next heaviest atoms being those of bismuth (208.0) and lead (207.1) ($O=16$). The study of radioactivity has peopled this gap with more than thirty unstable elements. Two other elements, potassium and rubidium, possess a feeble indication of a radioactivity of a peculiar kind, but it is far from proved that this radioactivity is of the same nature as in the case of uranium and thorium, and for the present it need not be further considered. To-day, however, some thirty-four distinct types of radioactive matter are known with certainty, each with a definite and characteristic kind of radioactivity. Radioactivity is an atomic phenomenon, and each of these new types is fully entitled to be considered a new atom, and therefore a new chemical element. These are all derived from natural minerals containing uranium or thorium, and their isolation and identification as separate individuals are due entirely to the delicacy of radioactive methods,

which far surpass in this respect the utmost that the spectroscope can accomplish.

New Radio-Elements.—The first discovered of these new radio-elements were radium,² polonium, and actinium.³ They were derived from the working up of large quantities of pitch-blende (impure uranoso-uranic oxide, U_3O_8) from the Joachimsthal mine in Bohemia. Latterly a similar study of the thorium minerals has resulted in the isolation of similar new radio-elements of technical value, mesothorium and radiothorium. In all of these the radioactivity of the material is relatively enormous compared with that of uranium, and is more or less permanent. Of these new types of chemical elements only radium and its first product, the radium emanation, have been thoroughly examined in the same way as the ordinary elements. For these the atomic weight has been directly determined and the spectrum mapped. All the others either exist in too small quantity for this yet to have been possible, or are incapable of being separated from the inactive elements with which they are always associated in the mineral. In radium no diminution of the radioactivity with time after separation has yet been observed, and the same is true of the common radio-elements, uranium and thorium, while in the others a slow decay over a period of years takes place. Besides these, numerous other types of radioactive matter are known which are more transitory, lasting in the various cases only months, days, hours, minutes, or even seconds.

Some of the earliest of these types of transitorily radioactive matter to be studied were the emanations.⁴ The radio-elements, thorium, radium, and actinium, but not uranium or polonium, produce, in addition to radiations, what are known as radioactive emanations, and the two phenomena must on no account be confused. A current of air passed through the first-named substances, preferably in solution, carries away radioactive gases or "emanations" which give out rays of similar kind to those from the other radioactive elements. The radioactivity of the emanations is, however, transient, lasting a few days in the case of radium, a few minutes in the case of thorium, and a few seconds in the case of actinium. The emanations can all be condensed out from the air at the temperature of liquid

air. Chemically they resemble the rare gases of the argon group, in that it is impossible to absorb them by chemical reagents or cause them to enter into chemical combinations. The emanations all have the power of imparting radioactivity to solid objects coming in contact with them. This "active deposit" (also called the "induced" or "excited activity")⁵ again is transient, decaying according to regular laws at characteristic rates in the three cases. That from thorium lasts a few days, whilst that from actinium and from radium lasts a few hours before the decay is complete, the imparted activity from actinium decaying slightly more slowly than that from radium.

Radioactive Change.—A chemical examination of the radioactivity of thorium revealed the following remarkable facts. Simple precipitation of the thorium from its solution gives thorium hydroxide, from which the major part of the radioactivity is found to have been removed. The α -radiation is much enfeebled, and the substance has completely lost the power of producing the radioactive emanation. The solution from which the thorium had been precipitated possesses the whole of the emanating power of the original solution, and on evaporation and ignition, to expel ammonium salts, gives a minute residue containing the whole of the radioactivity which the thorium has lost. This new radioactive substance separated chemically from thorium was termed thorium X. The activity of the thorium X is, however, only transient. In the course of a month it completely disappears, decaying to half its initial value in four days. The emanating power disappears at the same rate. The thorium hydroxide, however, at first but slightly radioactive, *recovers* its radioactivity and emanating power just as fast as that of the thorium X decays. In a month its activity regains its old value. Now a fresh treatment with ammonia separates anew a fresh amount of "thorium X" of the same activity as the first. Thorium X is a short-lived radioactive product of the thorium, which itself produces the gaseous emanation, and the emanation in its turn produces the active deposit responsible for the "excited" or "induced activity." The case has been treated at length because it was the first "disintegration series" to be elucidated, and is typical of all radioactive changes.⁶

As a result of these and similar observations, a complete theory of radioactivity was put forward which is now universally accepted.⁷ The radio-elements are unstable and change spontaneously, the change being accompanied by the expulsion from the original atom of "rays" and the production of a new type of radioactive atom. The latter is often very much more unstable than the parent element, and changes again with expulsion of rays and formation of another new atom. This process of successive changes proceeds often through a great number of steps. Thus an α -ray is expelled in the change producing thorium X, the thorium X atom expels another α -ray and changes into the gaseous emanation, the emanation atom expels another α -ray and changes into the non-volatile matter constituting the active deposit, which in turn undergoes further changes of precisely similar type. The extension of this view has gradually included all the known phenomena of radioactivity. The thirty new types of radioactive matter before mentioned which occur in the uranium and thorium minerals are all almost certainly produced from either uranium or thorium by this process of successive changes. Lacunæ still remain to be filled. The production of radium and of actinium from uranium has not yet been directly observed, but there is strong indirect evidence that it occurs, and that time alone is required for the experiments to yield positive results.

Very definite conclusions have been established as to the precise nature of the atomic disintegration. In spite of very great differences in the stability of the various radio-elements, the periods during which they exist varying from thousandths of a second up to geological epochs of time, all the changes are of the same type. The rate of change varies enormously, but the changes all obey the same law as that of a monomolecular reaction. As expressed by Ostwald in words, this is: "As time increases in arithmetical progression, the quantity of substance decreases in geometrical progression." This is the simplest law possible. The rate of change at every instant is proportional to the quantity remaining unchanged at that instant. It has been established that radioactivity, so far as the individual atom is concerned, is an instantaneous phenomenon. Before and up to the actual moment of disintegration the atom of the radio-element is in

no way distinguished from the atom of an inactive element. After the disintegration has occurred, the new atom produced is in no way different from an ordinary atom until it in turn again disintegrates. But in any mass of a radio-element the atoms do not all disintegrate at the same instant, so that the emission of rays appears at first sight to be a continuous phenomenon. The simple resolution by a lens of the glow produced by α -rays on a phosphorescent screen of zinc sulphide, as in the spintharoscope of Sir William Crookes,⁸ is sufficient to show that the emission of the radiation is perfectly discontinuous.

Analysis of the Radiations.—The rays from the radioactive substances have been proved by physical methods to be, or to arise from, electrically charged particles projected from the substance radially in all directions with great velocity.⁹ This forms an essential part of the theory of atomic disintegration. Three types of radiation are distinguished. They are, in order of penetrating power, the α -, β -, and γ -radiation, the α -rays being very feebly penetrating, but by far the most energetic and important type.

Three main effects produced by all the rays more or less in common are chiefly used in their detection and measurement. The rays act on the photographic plate, cause certain fluorescent substances to glow, and ionise the air and other gases. Photographically the α -rays have slight action, while their ionising action is enormous compared with that produced by the other two types. The β - and γ -rays possess, relatively to the α -rays, rather feeble ionising action, but are chiefly operative in the photographic actions, the action of the γ -rays being always very feeble compared with that of the β -rays which accompany them.

Different fluorescent substances behave differently to the three types of rays. For the α -rays a preparation of zinc sulphide is most sensitive. For the β - and γ -rays, barium and other platinocyanides and willemite (zinc silicate) are the fluorescers usually employed. Magnesium platinocyanide, which responds brilliantly to X-rays, is little affected by β - and γ -rays. The scintillations shown by a lens in the fluorescence of zinc sulphide under the α -rays are due to the individual impacts of the α -particles, each impact causing a separate flash of light. This is one of

the methods by which the actual number of α -particles expelled from a radioactive substance in a given time has been directly counted.¹⁰

The three types of rays are distinguished in the first place by their power of penetrating matter. The α -rays are most easily absorbed. None are able to penetrate a piece of ordinary paper or more than 8.6 centimetres of air at atmospheric pressure. The β -rays go through thin metal foils with ease, but are for the most part absorbed by a millimetre of lead. The γ -rays are able to pass through great thickness of metal without complete absorption. The more penetrating types are those of the thorium and radium series, and for these every 1.4 cm. of lead cuts down the radiation to about half its initial value. The three types are distinguished also by their behaviour in the magnetic field. The α - and β -types are deviated, the γ are not. The β -rays, like the cathode-rays or radiant matter of the Crookes tube, being negatively charged and almost mass-less, are readily coiled into circles or spirals by a magnetic field. Some of the β -rays travel with a velocity very nearly that of light, which is many times greater than that of the cathode rays, so that the β -rays are considerably more difficult to deviate than the latter. The α -rays, being positively charged, are deviated in the opposite sense to the β -rays, but owing to the mass being much greater than that of the β -rays, the deviation is extremely slight, and refined experiments with very powerful magnetic fields are necessary to detect the deviation.

α -Rays.—In all cases where the disintegration is accompanied by the type of radiation known as the α -rays, the atom suffers a definite loss of its mass, part of it being projected as a separate atom with great velocity. It was predicted from the association of helium in the minerals containing the radio-elements that one of the ultimate products of the disintegration was the element helium. In 1903 the continuous production of helium from radium was directly observed by spectroscopic methods.¹¹ The α -rays were shown first to consist of positively charged particles of atomic size expelled with a velocity about one-tenth that of light. The existence of this charge renders the particle liable to deviation by electric and magnetic forces. By the

application of these and similar physical methods of attack, data were gradually accumulated from which the atomic weight of the radiated particle constituting the α -rays could be determined. This proved to have the value 4 in terms of hydrogen as unity. The α -particle carries two atomic charges of positive electricity; that is to say, it is a divalent ion. The identity of the α -particles with the helium produced in radioactivity has been cleverly established by experiments in thin-walled glass tubes of capillary bore, perfectly gas-tight, but so excessively thin that the α -rays are able to penetrate the walls. Such a tube, filled with the gaseous radium emanation, generates helium in the surrounding space *outside* the tube, though when filled with helium none escapes. If the tube is wrapped round with lead-foil the helium is driven into the lead, and can be so stored. On melting the lead in a perfect vacuum the helium is liberated, and can be detected by its spectrum.¹²

The α -rays have some very remarkable properties, which are unique to this type of radiation. They travel a definite distance, known as the "range" in any homogeneous medium, before being absorbed. The various types of α -rays expelled in the different disintegrations differ from one another *only* in the initial velocity of expulsion, which varies from 7.5 % of the velocity of light for the α -particles of thorium C to about 5 % for the α -particles of uranium. It has been proved that all the α -particles expelled in any one type of disintegration travel with exactly the same velocity.¹³ This velocity is gradually diminished to very nearly the same extent for each particle in passage through a homogeneous absorbing medium, until the "critical velocity," 2.7 % of that of light, is reached. The ionisation produced, and the same is true generally of the photographic and fluorescent effects in any given length of its path, *increases* as the velocity of the particle diminishes down to the critical velocity, when all effects cease with great abruptness, and the α -particle is "absorbed" or passes beyond all means of detection. Hence the "range" of the α -particle, which is proportional to the cube of its velocity, is an important constant, characteristic of the type of disintegration in which it is expelled.¹⁴ The ranges given for the α -rays are taken for the most part from the annual tables of radioactive constants published

in *Le Radium*.¹⁵ They refer to a temperature of 0° C. and a pressure of 760 mm., and are directly proportional to the absolute temperature and inversely proportional to the pressure.

A connection exists between the range or velocity of the α -particle and the period of the change in which it is generated. The longer the period the shorter is the range. This is further considered in the next section.

Placing equal numbers of atoms of different materials in the path of the α -rays, it is found that all substances absorb α -rays proportionally to the square root of the atomic weight of the substance, if elementary, or to the mean of the square roots of the weights of the constituent atoms, if a compound or mixture. The range in air at N.T.P. varies between the limits of 8.6 cm. and 2.6 cm., so that knowing this range, the range in any other substance simple or compound can be calculated.¹⁶ In mica the fastest α -particle known travels 0.040 mm. The pleochroic halos occurring in certain micas are due to microscopic inclusions of radioactive substances, the α -rays of which have, over geological epochs of time, caused spherical shells of blackening around the inclusion, the ranges of which correspond to the various ranges of the α -rays emitted. From the diameter of these halos the thorium inclusions can readily be distinguished from the uranium inclusions, which are somewhat smaller.¹⁷

Scattering of α -Particles: Internal Structure of the Atom.—At first it was thought that the α -particles, in penetrating the atoms they encounter in their path, plough their way straight through without perceptible deviation. When it is considered that the α -particle is itself an atom of helium of mass 4, it is clear that in the passage of α -particles through matter we are witnessing a veritable interpenetration of one atom by another, a phenomenon absolutely new in science and of the most momentous import. A closer study has made it clear that, although the overwhelming majority of the α -particles do in fact steer a nearly straight course in their path through the atoms they encounter, they are subjected to continual slight hither and thither deflections, especially towards the end of their range, which quite perceptibly, though slightly, scatter an originally parallel beam, and cause it to broaden and become more diffuse the

farther it travels. Nevertheless, if the atoms were in reality the hard solid spheres occupying space to the total exclusion of everything else, which the older phenomena of physics and chemistry made appear probable, the almost undeviated flight of α -particles right through them would be impossible.

But this is not the whole truth. Thousands of α -particles so pass, each through thousands of atoms in their paths, but an occasional one is violently swung out of its path by a single exceptionally close encounter, and may even emerge from the side it entered. This occasional single scattering, as it is termed by Rutherford, is very different from the slight hither and thither deflections according to the laws of probability which also take place. It gives us our first experimental evidence of what the interior of the atom really is. It shows that practically the whole mass of the atom must be concentrated in an excessively minute volume or nucleus, which Rutherford estimates as of the order of a thousand million million times less than the apparent and usually accepted atomic volume.¹⁸

This nuclear theory of atomic structure of Rutherford, founded initially on the scattering of α -particles, though still in embryo, has already proved itself of great assistance in co-ordinating various phenomena, and a very brief description of its central idea may be included here. The further experimental basis of it rests on the generalisation, later to be considered, connecting the expulsion of α - and β -particles and the position of the product in the Periodic Law, the researches on the high-frequency or X-ray spectra of the elements, and the nature of the β -rays dealt with in the next section. It is supposed that the successive places in the Periodic Table from hydrogen to uranium, probably 92 in all, correspond with successive unit increments in the nett positive charge of the atomic nucleus, from 1 to 92. Around this nucleus, in some unknown way, and occupying the atomic volume as usually understood, circulate a number of negative electrons equal to the nett positive nuclear charge, or "atomic number," as it is called. Whereas all the older phenomena encountered in the study of matter are concerned solely with the negative electronic outer system, and usually only with the outermost ring or shell of it, the newer phenomena of X-rays and radioactivity are concerned with

the innermost region and the positive nucleus respectively. The atomic number—that is, the magnitude of the central positive charge on the nucleus—rather than the mass controls the chemical and physical properties of the atom, so that atoms of different masses but of identical atomic number are identical in chemical properties. Numerous such chemically identical elements, thanks to the systematic study of the products of radioactive change, are now known, and will be considered in the sequel. It appears, therefore, that the fundamental idea of the nature of the chemical elements may be false. Chemical analysis may not be an analysis of matter into atoms homogeneous as regards mass, but rather homogeneous as regards the nett nuclear positive charge. In the great majority of cases, no doubt, only one atomic structure of a given atomic number may be sufficiently stable to exist permanently, and hence the majority of elements may be homogeneous as regards atomic mass. But it appears likely that in some cases more than one atom of certain atomic numbers may be stable, and such atoms would not necessarily have the same mass, though they would appear as homogeneous elements to every test chemical analysis could impose.

β - and γ -rays.—The β -rays also consist of expelled particles, but in this case the particles are not atoms of matter, but free atoms of negative electricity or “electrons.” The velocity with which the β -particles move varies in different cases up to a maximum almost indistinguishable from that of light. They have considerable penetrating power, and are able to traverse thin plates of metals and other substances before being completely absorbed.

It is probable that, as in the case of the α -rays, each disintegrating atom expels one β -particle only, but the velocities with which the individual β -particles escape vary widely from atom to atom of the same radio-element. In a magnetic field the β -rays are coiled up into circles of smaller or greater radius according as their velocity is small or great, and it is possible to analyse a beam of β -rays by this means according to their velocity. As in the case of the α -rays, the rays lose velocity in their passage through matter, and, in order to obtain the initial velocities, it is necessary to work with preparations, such as the active deposits, that can be

obtained free from other matter as invisible and unweighable films deposited on surfaces, in which the absorption of the β -rays in the preparation itself is negligible. The β -rays starting, for example, from the surface of a layer of uranium oxide, possess a higher velocity than those that come beneath the surface, and, even if such rays were homogeneous initially, they would be heterogeneous as they emerged from such a preparation.

The results of such analysis have been to show that in no case are the β -rays expelled initially all with the same velocity.

In some cases—for example, those of uranium X, mesothorium 2, and radium E—resolution by a magnetic field into rays of different velocity has shown that there is a more or less continuous distribution of velocity among the individual rays. The “magnetic spectrum” is, so far as it has yet been resolved, continuous. For other β -rays distinct groups of rays of definite velocity have been observed. The “magnetic spectrum” shows “lines” corresponding with rays of definite velocity. But such lines are frequently very numerous. In the β -rays of radium B and C, no less than 16 lines for radium B and 48 lines for radium C have been tabulated, the first between 0.365 and 0.832, and the second with a range up to 0.986 of the velocity of light.

According to Rutherford, there is evidence that the energies of the successive rays in the magnetic spectrum differ by a constant quantity. Thus for 29 lines of radium C the energies were integral multiples of the same fixed quantity, the integers being the alternate odd ones from 59 to 47, and, with the exception of 45, every integer between 46 and 24. It is possible to suppose that the initial energy of each β -ray from a single radio-element is the same. The β -rays originate in the central positively charged nucleus of the atom, and in escaping therefrom have to pass through the successive rings or shells of surrounding negative electrons, in which process energy is successively abstracted *in quanta* which, possibly, reappears as γ -ray energy. The subject, it will be seen, is full of interest, and promises to shed fresh light on the nature of radiant energy, in the same direction as the quantum theory of Planck and the essential identity of γ -rays and light, about to be discussed, have already effected so many revolutionary changes.¹⁹

A third type of radiation, the γ -radiation, usually accompanies the β -radiation. For long it was supposed to be a secondary electro-magnetic disturbance in the ether, due to the motion of the β -rays, and the same explanation embraced also the relation between X-rays and cathode rays.

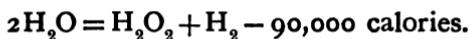
After having been challenged by a rival hypothesis,²⁰ which ascribed to the γ -rays a discrete nature like the β -rays, with the difference that the discrete particle was supposed to be a neutral pair or doublet, consisting of one negative and one, still unknown and probably non-existent, positive electron, the original theory has triumphed. X-rays and γ -rays are light waves, the wave-length being of the order of a thousand times less than that of visible light. We owe this advance to the fact that, though they are of too short wave-length to be resolved by any mechanically ruled grating, in crystalline solids the ordered disposition of the atoms in space serves the same function as the ordered ruling of a grating to ordinary light, the spaces between the atoms being just of the right dimensions to diffract the X-rays and γ -rays.²¹ By this diffraction of the rays, in their passage through crystals of rock-salt, diamond, and so on, their wave-lengths have been determined. It ranges from about 10^{-8} cm., or 1 Ångstrom unit, for the soft or non-penetrating γ -rays of radium B, to 0.7×10^{-8} cm., for the very penetrating γ -rays of radium C.²²

More exhaustive study has recently shown that the first rough division by penetrating power is not sufficient. Now, both β - and γ -rays are recognised of all degrees of penetrating power, from that possessed by the α -rays up to the most penetrating types, to which at first our knowledge was confined.²³ The first analysis having been made by successively weeding out the less penetrating types by causing the rays to pass through thicker and thicker screens, naturally the β -rays of the same order of penetrating power as the α -rays, and the γ -rays, similar in these respects to β - or even α -rays, were overlooked. A β -ray, whatever its penetrating power, is always a single free-flying electron, its velocity, only, being different, those moving most rapidly being the most penetrating. So also with the γ -rays, the wave-length or its reciprocal, the frequency, fixes the penetrating power—the shorter the

wave-length, or greater the frequency, the greater is the penetrating power. But it is a convenience to distinguish the less penetrating varieties of β - and γ -rays from the longer known, and therefore still regarded as typical, penetrating varieties. For this reason the feebly penetrating varieties are throughout characterised by brackets, thus : (β), (γ). But it must be understood that the distinction is made for practical convenience only, and has no theoretical significance.

Lastly, when the velocity of the β -ray falls below a certain critical value it fails to ionise gases and can no longer be detected by this test, but solely by the negative charge which the rays carry. To such rays the name δ -rays has been given, but they are not further considered here. They come into evidence as a secondary radiation, when α -rays bombard matter, but from their nature and absence of penetrating and ionising power, they would only make their presence felt in experiments in a vacuum.

Chemical Action of the Rays.—In addition to the photographic effect, the rays produce many other chemical actions. The most notable is the decomposition of water, which renders it dangerous to seal up radium or other highly radioactive preparations, either in solution, or in an imperfectly dried condition for indefinite periods, owing to the possibility of the vessel bursting and the contents being scattered. For pure radium salts dissolved in water, under which condition the α -rays are operative, the amount of hydrogen and oxygen evolved is some 15 c.c. per day per gram of radium. Much the same rate would be initially produced from the emanation dissolved in water. When the β - and γ -rays only are operative, as when the radium or the emanation is contained in a sealed glass tube immersed in water, the evolution of gas is 0.115 c.c. per day per gram of radium, and it consists of pure hydrogen, hydrogen peroxide being also formed, in accordance with the equation—



This may account for the fact that in the mixed gases evolved from a solution of radium, the hydrogen is always in slight excess. If the rays from the emanation act on water

vapour this excess of hydrogen attains 50 % by volume. Whereas for ice at -180° there is no excess of hydrogen, but the amount of decomposition is only 5 % of that which would be produced in liquid water. Conversely, when hydrogen and oxygen, in presence of phosphorus pentoxide, are exposed to the rays, the gases combine to form water.²⁴

The same type of reversible reactions occur with most other gases. Ammonia is rapidly decomposed, whereas a mixture of hydrogen and nitrogen, in presence of a reagent that absorbs ammonia, contracts in volume. Carbon dioxide is decomposed into carbon monoxide, carbon, and oxygen, whereas carbon monoxide forms carbon dioxide, carbon, and oxygen. Nitrogen, in presence of oxygen, is oxidised. If air, containing emanation, is stored over mercury, nitrous oxide will be found to be formed. No doubt the formation of combined nitrogen from the air, hitherto attributed to silent electric discharges, is largely due to the radium emanation and other radioactive products invariably present in minute amount in the air.

The general chemical action of the rays seems to be of the nature of a shattering of the molecule and the transient formation of free atoms, which, as in the so-called nascent state, readily recombine and enter into new combinations, which the same elements in the molecular condition are unable to effect. It would appear also, at least as a first approximation, that an extension of Faraday's law of liquid electrolysis controls the action of these rays on the quantitative side. The rays in the gas produce a certain amount of ionisation. If this amount be expressed in faradays, it will be found to be of the same order as the amount of chemical action expressed in moles. Thus, in the decomposition of liquid water, for example, the number of molecules decomposed is approximately the same as the number of pairs of ions formed when the rays traverse a gas. This holds even more accurately when the gas in question is water vapour or electrolytic gas rather than air. The numbers of ions produced in various gases by the same rays are not very different, varying over a range of from 1 to 1.3.

Other chemical actions of the rays which have been studied are the decomposition of hydrogen peroxide, the

liberation of iodine from iodides of the alkali-metals, especially in acid solution, the reduction of silver nitrate solution to metallic silver, the oxidation of organic acids, such as acetic acid, and of ethyl alcohol to acetaldehyde and acetic acid, the inversion of sterilised solutions of cane sugar and many others. Many of these changes are produced by ultra-violet light, and it must be remembered that the quantities of material decomposed by the radium rays is always relatively very small.²⁵

Lastly, the colouring action of the rays on common glass and on many gems may be referred to. Ordinary soft laboratory glass is coloured usually a purple tint, but sometimes brown according to its composition. Hard glasses are coloured brown. Diamonds of the purest water are probably not coloured (Beilby), but ordinary stones frequently assume more or less brilliant colours, in one remarkable case, observed by Sir William Crookes, a very fine green being developed. Pure silica is rapidly disintegrated under the rays, and for this reason should not be used to contain radium preparations permanently. Probably owing to the formation of nitric acid from the air, paper and fabrics in which radioactive preparations are wrapped are reduced to powder in the course of time, even when the radium is in sealed glass tubes.

Quantities of Material capable of being worked with in Radio-Chemistry.—Radioactivity being the manifestation of a spontaneous process of atomic change or transformation, the least amount of any type of radioactive matter that can be detected is the least amount in which this change can be detected. So that if the type changes rapidly, proportionately less of it will give a detectable effect than if it changes slowly. Even for the most slowly changing types, thorium and uranium, the sensitiveness of the radioactive tests are considerably greater than, though of the same general order as, the sensitiveness of the usual chemical reactions of these elements. For the most rapidly changing types, the presence of a few hundred individual atoms is sufficient to give a clear radioactive effect. The significance of this will be the better understood when it is remembered that the most delicate spectroscope test of matter known requires not less than many millions of millions of individual atoms.

On this account and because of the evanescent character of the materials, the chemistry of the radio-elements has been described as a "Chemistry of Phantoms," and by those unfamiliar with the subject it has been supposed that the study of such substances can have little in common with chemistry in general.

But it is important to note that, just in proportion as the rapidity of the change is the greater and the quantities of material available in consequence become inappreciable to the older methods of study, the newer methods become applicable. For these depend upon the radioactivity, that is, on the part of the material changing, not on the total amount present. Chemical analysis depends on the total quantity of the material, but radioactivity depends on this quantity divided by the period of average life. In other words, the more evanescent the material and the less of it is available to work with, the less can be worked with, so that the minuteness of the quantities presents a less difficulty than might be supposed.

Although the actual quantities of matter producing radioactive effects are usually infinitesimal, they are, however, always capable of being calculated from the magnitude of the radioactive effect and the period of average life of the radio-atom producing the effect. Thus the calculated quantity of polonium in a radium mineral is 1 milligram of polonium for every 14 tons of uranium. It is possible therefore to know beforehand, in almost every case, whether or not sufficient of the material is present to warrant attempts at its separation and the examination of its spectrum and atomic weight. This is indeed very rarely possible, but the subject has been attacked by new methods, and surprisingly complete information has already been gained of the chemical nature and reactions of these ephemeral elements. A special branch of chemistry, which may be appropriately termed "Radio-Chemistry," has come into existence, the scope and methods of which are largely peculiar to itself. The results, however, throw new light on many old chemical problems, and constitute an advance, the first, perhaps, made since the time of Dalton, in our conception of the real nature of a "chemical element."

RADIOACTIVE CONSTANTS, PERIODS OF AVERAGE LIFE AND RADIOACTIVE EQUILIBRIUM

The Radioactive Constant.—The most important property of a radio-element is its period of average life or its rate of change. This is not only a natural fundamental time-constant, serving to identify the particular element in all circumstances, and conversely affording an absolute standard of time independently of the sequence of astronomical events, but it fixes also the whole character of the knowledge it is possible to obtain as to the nature of the radio-element. In the case of a rapidly changing substance, the period is determined by direct observation of the rate of decay of the radiation with time. For a single radio-element free from its parent, and therefore not being reproduced, the quantity in existence diminishes, owing to its disintegration, in an exponential manner with the time according to the equation

$$I/I_0 = e^{-\lambda t}, \text{ or } \log_{10} (I/I_0) = -0.4343\lambda t.$$

If the product of the disintegration is inactive or does not interfere, as is the case, for example, with polonium, the radioactivity decays also according to the above law. In the above equation, therefore, I_0 is the initial activity or the initial quantity, I , the activity or quantity after any time t , λ a constant known as the radioactive constant, and e is the number 2.71828. The physical meaning of the radioactive constant λ is the fraction of the total amount of radioactive substance disintegrating in the unit of time (provided that the time unit considered is so small that the quantity at the end of the time unit is not sensibly different from that at the beginning). The time required for one-half the radioactive substance to change is known as the period of half-change T , and is calculated from λ by means of the equation

$$\log 0.5 = -0.4343\lambda T.$$

Hence T is $0.6932 (1/\lambda)$, or $1/\lambda = 1.443T$.

Now it can be shown mathematically that in a system changing according to the law of radioactive change, the period of average life of the atom is $1/\lambda$. The term "period of average life" relates to the future life of the atom. It has nothing to do with and is not affected by the period the atom has already been in existence. Any time may be chosen as the starting point. The period of average life is the sum of the separate periods of future existence of all the individual atoms divided by the number in existence at the starting point.

There is thus a simple connection between the radioactive constant, the period of average life, and the period of half-change. Each of the latter periods has its conveniences in rapid mental calculation. Suppose it were desired to know the fraction of a mass of radium changing in a time so short that the total mass is not much diminished, say a few years. The period of average life of radium is 2440 years. The radioactive constant or the amount changing per year is $1/2440$ (which is usually expressed $\lambda(\text{year})^{-1} = 4.1 \times 10^{-4}$), and the fraction changing in any time, provided it is not too long, can be found from this by simple proportion. But if it were desired to find the amount of polonium (period of average life 196 days, period of half-change 136 days) remaining unchanged after say three years, the following application of the period of half-change would be useful. In n times the period of half-change the amount of a radioactive substance is reduced to $(\frac{1}{2})^n$. Three years is 8.05 times the period of half-change. Hence the amount of polonium remaining is nearly $(\frac{1}{2})^8$, i.e. $1/256$ th, and by the use of logarithms can be found at once exactly. It is worth remembering that in ten times the period of half-change the quantity remaining is less than 0.1 %, and in twenty times the period of half-change less than a millionth.

365
1895
136 1088 100

The periods of average life of the thirty-four radio-elements range from some thousands of millions of years, in the case of the primary radio-elements, uranium and thorium, to less than a millionth of a second in the case of the shortest, the existence of which, naturally, is inferred rather than directly demonstrable. The primary elements change with such excessive slowness that they preserve the

strain, as it were, of their more unstable successors throughout the ages. In a ton of the element uranium (10^9 milligrams) about one-eighth of a milligram disintegrates annually, and it is the disintegration of this infinitesimal quantity which, for a year, endows the whole of the ton of the uranium with its radioactivity. Compared with radium the radioactivity is, naturally, very feeble, but the radioactivity of one milligram of uranium, or even less, could, nevertheless, be detected with ease, by a suitable gold-leaf electroscope, taking perhaps an hour over the observation. A thousand-millionth of one-eighth of a milligram, reduced in the proportion of an hour to a year, is, therefore, the measure of the absolute quantity of matter actually disintegrating which is detectable by the electroscope. It does not much matter whether this quantity is a small or large fraction of the total radioactive matter present, so far as radioactive methods are concerned. As the illustration will serve to show, to any one pondering over it, it is the quantity divided by the period of average life, not the total quantity present, which is of importance.

Absorption of β - and γ -Rays.—It happens that some of the foregoing considerations are applicable in a totally different connection in radioactivity, and it will save repetition to refer to them incidentally here. The law of absorption of a homogeneous β - or γ -radiation is mathematically the same as that of radioactive change, on the assumption that the absorption is due to the abrupt stoppage of individual rays by each layer of the absorbing matter, and not to the gradual sapping of the energy of the whole beam. The absorption, or diminution in the number of these radiations, is proportional always to the amount of radiation remaining unabsorbed, and therefore follows the exponential law denoted by the equation

$$\frac{I_t}{I_0} = e^{-\mu t}$$

where I_0 and I_t are respectively the intensities of radiation initially and after passage through any thickness t , and μ is the "coefficient of absorption." The radiation is half-absorbed in a thickness T given by $0.693/\mu$. The reciprocal of the absorption coefficient $1/\mu$ is the "average path" of the individual rays, on the afore-mentioned hypothesis.

From the absorption coefficients the thickness of matter required to reduce the radiation to any required fraction of its initial value can be readily calculated, though it must be understood that these laws are not always exactly followed.

In the sequel, the absorption coefficients, μ , are expressed in centimetre units of length, for the metal aluminium for the β - and γ -rays and for the metal lead for the hard γ -rays. From these absorption coefficients the "average path" of the rays, and the thickness in which one-half is absorbed, are readily deduced. Knowing the latter thickness, T cm., it follows that in $2T$ cm. the radiation is reduced to one-fourth, in $3T$ cm. to one-eighth, and in nT cm. to $(\frac{1}{2})^n$. Thus, as an example, from the absorption coefficient μ (cm.)⁻¹, Al = 14, the average path of the ray in aluminium is $1/14$ th cm., the thickness required for half-absorption is about 0.5 mm., and the thickness for all but some 3% to be absorbed, about 2.5 mm.

The underlying hypothesis, that absorption is due to sudden stoppage of a proportion of the rays, the remainder proceeding with undiminished energy, is certainly not true in the case of the β -rays. But then neither are they homogeneous. These departures from the assumptions made in the mathematical theory, in part neutralise one another's effects. A homogeneous beam, suffering a continuous drain on all rather than the sudden stoppage of a part of the rays, would be absorbed more rapidly than the exponential law expresses, whereas a heterogeneous beam, in which the slower rays are being gradually weeded out by absorption, will be absorbed less rapidly than the exponential law expresses. In consequence, over moderate thicknesses, to the point at which the rays have been reduced in intensity to a few per cent. of their initial value, the exponential law usually holds for β -rays with very tolerable accuracy.

In the case of γ -rays, the exponential law holds nearly absolutely, probably, so long as the rays are homogeneous. In the most common cases of the hard γ -rays of radium and thorium, the law holds after the rays have traversed 1 cm. of lead or its equivalent, which is sufficient to weed out all the softer types of γ -rays present in the beam.

As regards different absorbing materials, in the case of all these rays as a rough first approximation, the absorption

may be regarded as proportional to the density of the substance. In the case of the β -rays the atomic weight as well as the density is of influence, metals of high atomic weight absorbing more strongly in comparison with those of lighter atomic weight than the density law would indicate. The "density law," that the absorption coefficient multiplied by the density of the material is the same for all materials, holds very nearly for γ -rays, very light as well as very heavy substances absorbing slightly more than this law would indicate in comparison with substances of intermediate density. The numerical value of the absorption coefficients depends also, sometimes to a considerable extent, on the particular experimental disposition employed.

Growth or Regeneration of Radio-Elements.—Resuming the subject of radioactive change, we have considered the exponential diminution of quantity of a single radio-element removed from its parent. The parent continues to disintegrate and produce the product that has just been separated, so that the latter commences to reaccumulate in the parent, whilst that separated commences to diminish and its activity to decay. Remembering that the mere act of chemical separation in no way affects the rates at which these radioactive changes proceed, it follows that just as fast as the separated product diminishes in quantity, so will the quantity of it, reaccumulating in the parent, increase. This is expressed by the relation $I_t/I_\infty = 1 - e^{-\lambda t}$, where I_t is again the quantity or activity after any time t and I_∞ is the final or "equilibrium" quantity, that is the quantity which finally will accumulate after an infinite time.

A changing substance is being regenerated. This is analogous to a leaky vessel being filled. When the rate of change equals the rate of production, or when the rate of leakage equals the rate of filling, no more accumulates. An equilibrium is produced, in either case, which the further passage of time no longer alters. If, in this state, the product is separated by a chemical operation completely, the equilibrium quantity I_∞ so separated starts to diminish, just as the initial quantity I_0 of the first equation did. The suffixes o and ∞ refer to the time, which is either o or ∞ , in accordance as the diminution of the separated product or its reaccumulation is being considered.

Radioactive Equilibrium. — In the three disintegration series there is a long succession of changes, A producing B, B producing C, C producing D, and so on. A, B, C, D, are all changing at different, usually vastly different, rates but all according to the simple exponential, or monomolecular law. The principle of radioactive equilibrium applies not only to a single product and its parent, but to the whole series from one end to the other. The radioactive disintegration series has been likened to a number of reservoirs of different heights, but of the same cross section, with capillary tubes of different sizes in the bottoms, supplied at one end with a steady flow of water which runs through the whole series, from the bottom of each reservoir into the top of the next. The steady flow of water in at the top represents the steady production of the first disintegration product from the parent. The period of the latter is of the order of thousands of millions of years, so that a small fraction of a thousand-millionth part changes annually. The diminution of the quantity of the parent is quite inappreciable over short periods, and consequently the supply of the first product is constant. The water flowing out from one reservoir to the next represents the proportion of one member of the series continuously being transformed into the next. The reservoirs with small outlets represent the radio-elements of long-life, the size of the outlet being inversely proportional to the life, or directly proportional to the rate of change. In these reservoirs the water accumulates till a certain "head" or pressure is produced at which the outflow and intake are equal. The law of radioactive change, that the amount transformed in unit time is proportional to the amount present, is the same as the rate of flow of water under the circumstances of the analogy, the amount flowing out being proportional to the amount of water in the reservoir, that is to its height or head.¹

A system of the kind described will, after the water has been running a sufficient time, come into equilibrium, and then the outflow and intake are for each reservoir throughout the series the same. In a radioactive mineral in which the products of transformation accumulate and do not escape, the amount of each product formed is equal to the amount transformed per unit of time throughout the series. Such is

¹ The law only holds strictly for reservoirs with capillary orifices.

known as radioactive equilibrium. But by definition of the radioactive constant λ , if the amounts of the successive members are $Q_1, Q_2, Q_3 \dots Q_n$ in radioactive equilibrium

$$\lambda_1 Q_1 = \lambda_2 Q_2 = \lambda_3 Q_3 = \dots \lambda_n Q_n$$

where $\lambda_1, \lambda_2, \lambda_3 \dots \lambda_n$ are the respective radioactive constants. Therefore the relative amounts of the successive members of the disintegration series in equilibrium are inversely proportional to their radioactive constants, or directly proportional to their periods of average life. Thus in uranium minerals there is a constant proportion between the quantities of the successive members. There is always about 3,200,000 times as much uranium as radium, that is, there are about 3.2 tons of uranium per gram of radium, so that if the period of average life of radium is known to be 2440 years, that of uranium is about 8,000,000,000 years. Again the period of average life of polonium is about 200 days. Consequently per ton of uranium there is present about one-fourteenth of a milligram of polonium.

In this way have been determined the periods of the very slowly changing elements on the one hand, and, on the other, the amounts of the very short-lived products in minerals. In the first place the period cannot be directly determined, but the relative quantities can. In the second case the periods can be determined, but the quantities are too small for direct measurement. For the radium emanation, which is a gas, the quantity, though infinitesimal, is capable of exact measurement. The volume of emanation in equilibrium with 1 gram of radium (element) is about 0.6 cub. mm. measured at normal temperature and pressure. The period of average life is known very exactly by direct observation of the rate of decay of its radioactivity. Hence for this one member both data are known, with the result that the same information can be obtained by calculation for most of the other members of the uranium series and for uranium itself. In the case of the thorium and actinium series the periods of the primary elements are less perfectly known. It should be stated that if "branch series" occur, these calculations are to a certain extent vitiated. The order of the results is, however, probably correct.

Some very important consequences, most easily illustrated

by specific examples, follow from the foregoing considerations. The period fixes not only the rate of decay of the radioactivity of a radio-element after it has been separated from its parent, but it also fixes the rate at which that radio-element is regenerated by its parent. Thus the β -activity of uranium X, when separated from uranium, decays with a half-period of 24.6 days. In the uranium the β -radiation is regenerated to the extent of one-half its normal equilibrium value in 24.6 days. In 49.2 days the β -radiation of the uranium X decays to one-fourth of its initial, while that of the uranium increases to three-fourths of its final value.

The equilibrium quantity, and the amount of radioactivity corresponding to this quantity, form the natural units by which the amount of substance, or of its radioactivity, are measured. In a uranium preparation the quantity of uranium X and the β -activity corresponding thereto increase with time until the equilibrium value is reached, and then do not further change. In seven times the period of half-change the quantity is within 1 %, in ten times within 0.1 %, in thirteen times within not much more than 0.01 % of the equilibrium. It is the period of the product, therefore, which fixes the rate of recovery as well as the rate of decay after equilibrium has been disturbed. A rapidly changing product is regenerated by the parent with corresponding rapidity, a slowly changing product with corresponding slowness. These considerations apply especially where the rate of supply of the product is constant, either by virtue of the long life of the parent or because the quantity of the parent is itself maintained by an earlier disintegration. If otherwise, and the product is longer lived than the parent, then of course, after the whole of the parent has disintegrated, the quantity of the product diminishes with its own proper rate of change.

Another consideration then comes in. If the period of the parent is very short, the radioactivity of the longer lived product may not be sufficiently great to be detectable. Thus an intense activity due to radium C, which decays rapidly, gives rise to a very feeble but enduring activity due to radium D and its products, the period of radium D being a quarter of a million times greater than that of its parent.

The effect of the α -activity of radium A deposited from the radium emanation on the walls of the containing vessel during a few minutes is comparable with that given by the emanation itself, whereas the emanation of thorium has to be maintained in a continuous stream for many hours before an effect of the thorium active deposit at all comparable with that of the emanation is produced on the walls of the vessel. This illustration is complicated, but the main reason is that in the first case the period of the parent is about 2000 greater than that of the product, whereas in the second example the period of the product is about 700 times that of the parent.

All of these illustrations are merely several examples of the fact already alluded to, that the quantity of radioactive substance divided by its period of average life fixes the number of atoms disintegrating per unit of time, and hence the degree of radioactivity. Since in the majority of cases the quantity of the matter concerned in the phenomenon is below the quantity detectable by any test except radioactivity, the quantity itself is of no importance. What is of importance is the radioactivity or quantity divided by the period.

No product of uranium X has yet been detected. In the theoretical scheme the product is an element, giving α -rays, which, from the magnitude of their range, by the relation about to be discussed, has probably a period of some millions of years. Hence, though an infinitesimal absolute quantity of uranium X, the period of which is about one month, will give an enormous radioactive effect, when this changes into its much longer-lived product, it passes altogether beyond the limit of experimental detection.

Physical Meaning of the Period of Average Life.—We may well inquire what it is upon which the period of a radio-element depends. This cannot be answered. The fundamental difficulty is to frame even a reasonable hypothesis which can account for the precise law of change, and this must, necessarily, precede the explanation of the meaning of the numerical constants which fix, in each case, the rate of change. We can say definitely that there is no gradual change of the disintegrating atom with lapse of time leading up to its ultimate destruction, because the period of average

life is constant. We may compare, for example, the period of a collection of atoms of radium emanation just freshly born, and none of which were in existence a minute before, with the period of another collection, say the millionth part of an initial quantity, all of which have survived at least fifteen weeks from their formation, or twenty times the average period of life. No difference in the rate of disintegration will be found between the two sets. There is no gradual ageing. Out of any collection of N radio-atoms λN are selected and change per second, but the remainder are left without perceptible alteration.

The Geiger-Nuttall Relation.¹⁴—Nevertheless there is one remarkable relation between the period of life and the character of the disintegration, as it is revealed by the velocity of the projected particle, in that the shorter the period the swifter is the α -particle that is expelled. In the case of the β -particle, it is probable that something of the same kind applies. But in the case of the α -particle a mathematical relation has been found to hold by Geiger and Nuttall. The range of the α -particle is proportional to the cube of its velocity. If the logarithms of the periods of the various radio-elements are plotted against the logarithms of the ranges of the α -particles they expel, straight lines result. The plotting of logarithms of quantities, rather than the quantities themselves, is a common graphical device to disclose a relationship existing between any unknown powers of the quantities involved. In the present instance, for example, obviously, only the slope but not the straightness of the lines would be affected, if, instead of the range, the velocities of the α -rays were employed.

This relationship is shown in Fig. 1, p. 28, in which the logarithms of the ranges are plotted on the horizontal axis and logarithms of the radio-active constants are plotted on the vertical axis.

This, still empirical, relationship may be destined to be of great importance in the problem of atomic structure. In each of the three disintegration series, of uranium, thorium, and actinium respectively, straight lines of similar slope, but not exactly superimposed, are obtained. The only clear exception is radio-actinium, the range of the α -particle being longer than that from actinium X, though its period

is longer. The divergence of thorium may be due to experimental error, this being, of all the points, the one most difficult to obtain with accuracy. The relationship enables us to calculate four unknown periods from the range of the α -particle. Thus, if the law holds good, the period of

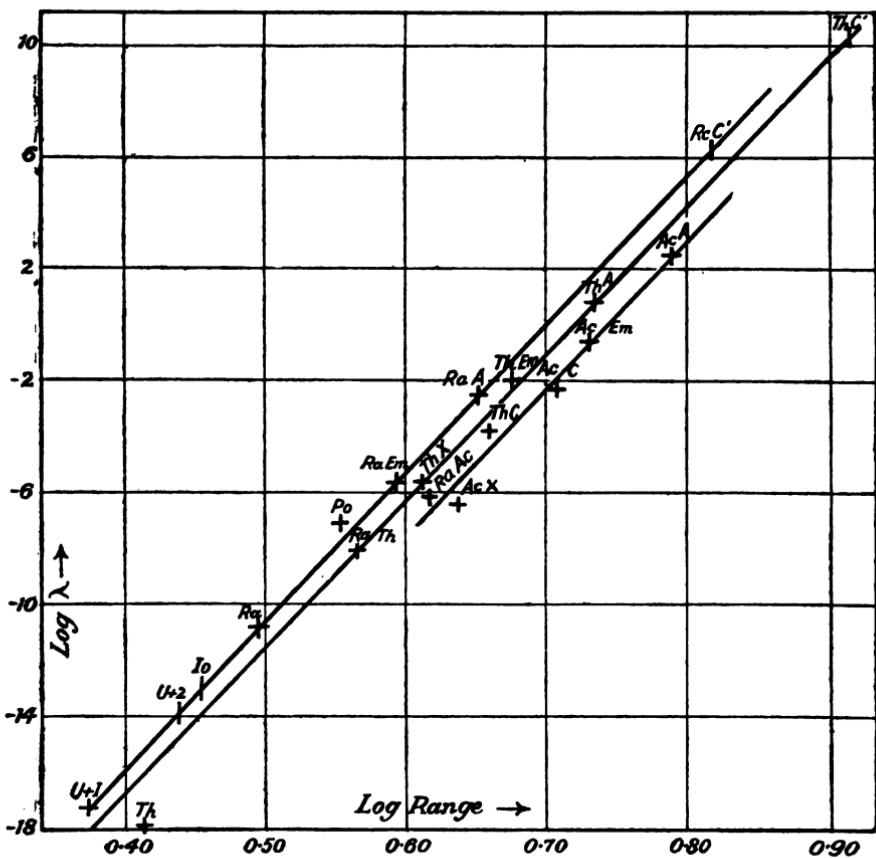


FIG. I.

average life of uranium 2 should be about 3×10^6 years, and that of ionium 3×10^5 years, periods too long for direct confirmation, as yet, though in the latter case the value agrees very well with what had been previously predicted from direct experiments. (See *Ionium*.) On the other hand, the extremely long range of the α -particles

from radium C' and thorium C' show that the periods corresponding are so short that the separate existence of the products producing the rays can only be inferred. Thus the period in the first case works out between 10^{-6} and 10^{-7} , and in the second case between 10^{-10} and 10^{-11} second. It might be thought hopeless to expect to know anything at all about the chemistry of such meteoric indications of elements. Nevertheless, their complete chemistry, no less than their existence, can be inferred!

As there will be no other opportunity of discussing the Geiger-Nuttall relationship, attention may here be directed to its most interesting feature. So long as any α -particle has the same range or velocity as any other, an equality which it is easy practically to secure by passing the swifter particle through a suitable thickness of absorbing material, they are indistinguishable in every respect. It would not be possible to distinguish, say, an α -particle of the thorium series from that of the uranium series. But the three straight lines in the above diagram are not exactly superimposable. For a given range the products of the uranium series are shorter lived than those of the thorium series, and these again than those of the actinium series. Hence, whatever be the meaning of this connection between range and period, it involves something that is the same for all the members of one series and is different in the different series. In other words, the atoms in their successive disintegrations preserve a feature distinctive of their origin. If this is confirmed it is highly significant, especially as it is contrary to what one might expect from the other evidence taken as a whole, and from the suspected, but not yet proved genetic interconnection of all three series. It would appear that some of these newer processes of radioactivity involve the conception of physical time in new ways, and may lead in turn to a deeper and more fundamental understanding of its nature.

ENUMERATION AND NOMENCLATURE OF THE RADIO-ELEMENTS — PRELIMIN- ARY DESCRIPTION OF THE DISINTE- GRATION SERIES.

THE thirty or more radio-elements known may be classified in various ways. They are all almost certainly derived from one of two primary parent elements—uranium and thorium. One of the commonest and most useful methods is to arrange them in two disintegration series, starting with these two elements in order of their production. The Table at the end of the book (Fig. 2) comprises all the radio-elements known, arranged in this way. It includes the period of average life of each member and the nature of the radiation expelled when it disintegrates and changes into the next member of the series. Inside the circles representing the elements are placed the atomic weights to the nearest unit, estimated, when not directly known, from the atomic weight of the parent and the number of α -particles expelled. There is an uncertainty as regards actinium, as the atomic weights throughout may well be four units less than is shown. The Roman numerals represent the family the element occupies in the Periodic Table.

In the uranium series, in addition to the main series, comprising ionium, radium, and polonium, there is a subsidiary series consisting of actinium and its products. The manner in which actinium comes to be produced is still not completely elucidated. Only a very small proportion of the uranium atoms disintegrating appear to go to produce actinium, by far the greater proportion probably going by the main series ultimately into polonium and probably lead. At some point in the series, which has not yet been determined, the atom disintegrating most probably has two modes of disintegration with different periods and different products, some of the atoms giving one and the others the other

product. (See Part II., pp. 22 and 32.) It is practically certain that the product of polonium is lead, although this has still to be established directly. The ultimate products of the thorium and actinium series also remain experimentally unknown, though their nature may now be inferred.

The nomenclature adopted has gradually been evolved, and is temporarily accepted until a complete scientific system can be agreed upon ; it has been frequently altered as new discoveries are made. At present the names themselves mean little or nothing. But there are good grounds for thinking that the three series are now nearly, if not quite, completely elucidated. The names chosen for the new radio-elements which were discovered before their position in the scheme was known have been usually retained, and sometimes new products in one series have been named by analogy to similar products in one of the others. In the case of the end products of disintegration of radium, which were worked out comparatively late, the system has been adopted of calling them in sequence radium A, radium B, radium C, &c. Sometimes it has been found that what has been considered a single change consists of two. Mesothorium 1 and mesothorium 2 constitute such an instance. In some cases the two separate products are not individually known, their separate existence being only indirectly inferred. This is provided for without disturbance to the rest of the names in the series, as in the case of the hopelessly short-lived radium C' and thorium C', already considered, to distinguish them when necessary from their parent substances radium C and thorium C.

Another possible method of classification of the radio-elements is based upon their periods of average life or rates of change. The parent elements, uranium and thorium, have the longest periods and change the most slowly, so that their chemistry does not differ at all from that of the inactive elements. If their products are then considered without reference to the series to which they belong, in descending order of their periods of life, we pass gradually through a series of substances in which the chemical methods of investigation become more and more different from those usually employed, and more and more peculiar to the study of radioactivity. The practical methods of preparation and

purification of the radio-elements are entirely controlled by the period of average life of the substance.

In a mineral the various members of each disintegration series exist in quantities directly proportional to the period of average life, so that a radio-element like, for example, polonium, with a period of life of less than a year, must be present in the mineral in far smaller quantity than radium, which has a period some thousands of times longer. With the short-lived substances, with periods of only a few hours or minutes, the actual quantities dealt with are always quite infinitesimal and quite incapable of being detected except by their radioactivity. A complete knowledge of the chemical behaviour of a radio-element in presence of any possible mixture of other elements, such as is involved, for example, in its extraction from the original mineral, is only required and is only possible for those radio-elements of period of the order of a year or more. This class comprises some nine radio-elements, which, arranged in descending order of period, are Thorium, Uranium, Ionium, Radium, Actinium, Radio-lead (Radium D), Mesothorium 1, Radiothorium, and Polonium. These are usually derived directly from the mineral, and indeed for most this is the only way of obtaining them, though radiothorium cannot and radio-lead and polonium need not be obtained in this way.

Radio-elements of shorter life than these cannot well be separated from the original minerals, if only because during the progress of the necessary chemical operations they tend to change as fast as they are separated from their parent substance. They are invariably obtained by separating the parent in as pure a state as possible, in the radioactive sense—that is, as free from other radioactive matter as possible—and allowing it to *grow* its short-lived products. For the separation of the latter it suffices to use means of separation capable of removing them from their parent on the one hand and from their own products on the other. Such operations are often relatively simple and rapid, and are often effected by adding a sensible quantity of an inactive substance which has a chemical resemblance to the radio-element required, which is only present in infinitesimal amount, and so using the former as a vehicle in the separation of the latter. Thus uranium X is prepared from a

purified uranium salt which has been kept a few months since preparation, and has regenerated its full equilibrium quantity of uranium X. Thorium X is prepared similarly from pure thorium salts (which always contain radiothorium, the immediate parent, in considerable quantity), and so on.

In the case of the two last-mentioned members of the first class, radiothorium and polonium, the first cannot be separated chemically from thorium, and so must be obtained from its parent mesothorium (which is separable from thorium) after it has been prepared for some time, while a valuable alternative source of polonium, instead of obtaining it direct from the mineral, is an old preparation of radio-lead in which polonium has been regenerated with lapse of time. Radio-lead, again, may be obtained from an old radium preparation which has been suitably preserved. It is, in the first place, a question of period. The second method involves a wait the longer and more tedious the longer the period of the product to be separated.

A certain regularity is observable in all the series in the periods of the successive products, which become, as a general rule, more and more unstable as the changes proceed. For the α -ray changes this is most marked. The first six α -ray giving members of the uranium series show a regular decrease of period from 8×10^9 years to 4.3 minutes, the first five of the thorium series from 4×10^{10} years to 0.2 second. The same is true for the actinium series for the first five α -ray giving members, and further discovery may make it true for the supposed α -ray giving parent of actinium also. It is probable that at the head of the series, as the direct parent of actinium, is an α -ray product, the life of which is so long that, as yet, it has eluded discovery (see p. 83). For these first portions of the three series just considered there exist only six β -ray giving products, two in each series, and they are all of relatively short period, the longest being mesothorium 1, 8.9 years, and the shortest, uranium X₂, 2.2 minutes.

In the latter part of the thorium and actinium series the longest lived product has a period of only 15 hours (thorium B), and over the corresponding part of the uranium-radium series there is no representative with period longer than 38.5 minutes. But radium D, which corresponds with the

last members of the other series, is not entirely stable, and in the completion of this series there are two moderately long-lived members, radio-lead and polonium, not represented at all in the other two series.

But neglecting these, which seem to arise in a final recrudescence of activity after stability has been very nearly reached, we may say broadly that the whole of the elements of period greater than a year—thorium, uranium, ionium, radium, actinium, mesothorium I and radiothorium—are at the beginning of the series. We have already seen that, excepting the last, these are the only ones it is necessary to separate directly from the minerals. All the products subsequent to these, and also radiothorium and four others in the early part of the series, are prepared by regeneration and separation from the pure parent. Radio-lead and polonium, as already discussed, are capable of separation by either method.

But for another reason it is natural to so divide the series into two, for the purposes of general classification. After six changes in the uranium, five in the thorium, and two in the actinium series, the products after passing from the character of acidic metals to basic metals, as represented by the sequence uranium, thorium, actinium, radium, now assume the gaseous form, and these gaseous products are known as the emanations. The preceding steps have been analogous to the passage from vanadium to calcium, through titanium and scandium, or from niobium to strontium, through zirconium and yttrium. But this next step is analogous to that from calcium to argon, strontium to krypton, or barium to xenon. Thus the division of the disintegration series into pre-emanation and post-emanation members, dictated by convenience, corresponds with the division in the Periodic Table, at the end of one long period and the beginning of the next.

The point of practical importance is that these products, being gaseous at ordinary temperature, actually separate themselves under suitable conditions without any chemical treatment at all. The whole of the succeeding products, with the two exceptions in the radium series already noted, being quite short-lived, they can all be "grown" in a form already separated from all inactive matter, without

chemical operations, and can be collected by purely physical methods.

Hence the problem of the separation of radioactive minerals resolves itself into the separation of some seven parent elements. From these all the others can be conveniently grown as required, the larger number of them very conveniently *via* the volatile emanation. It will be convenient to consider the latter process first, which is the first step in the separation of some sixteen, out of the total of thirty-four individual radio-elements that exist.

PHYSICAL METHODS OF SEPARATION.

The Emanations.—The first emanation to be discovered was that of the thorium series.⁴ Thorium compounds are sharply distinguished from uranium compounds in giving out a radioactive emanation, a gas emitting α -rays, which diffuses away from the compound and, when carried by currents or draughts of air, produces radioactive effects away from and out of the direct line of fire of the preparation itself. The gradual accumulation of this emanation inside the electroscope or measuring instrument causes the leak due to the preparation to increase for the first few minutes after a thorium preparation is inserted. The emanation escapes freely from the thorium compound under some circumstances and with difficulty under others, and the general conditions which favour or retard the escape may first be dealt with.

The actinium and the thorium emanations are short-lived and are usually worked with by passing a continuous stream of air or other gas through the preparation, which at once effects the desired separation. Solid preparations vary enormously in the ease or difficulty with which they part with their emanation. As regards thorium, the best emanators in the solid condition are the hydroxide and carbonate. After ignition to oxide, the emanating power is greatly reduced, the more strongly the compound is ignited, until, after ignition at a white heat, it may be reduced to a few per cent. of that of the unignited compound. Solid nitrate of thorium retains its emanation as tenaciously as the fully ignited oxide, and the oxalate and sulphate are both poor emanators.⁵ As regards radium, the bromide allows more emanation to escape than the chloride. From the sulphate, and, to a less extent, the carbonate, but little escapes from the solid. Apparently identical compounds may, however, in this respect exhibit a marked variation in behaviour.

From what has already been said, it will be understood that the rate of formation of the emanation from any given quantity of radioactive material is totally independent of all physical or chemical considerations. It is the rate of escape from the solid substance which varies so widely with the chemical nature and physical conditions.

These differences disappear when the substance is dissolved. Bubbling a rapid stream of air through a thorium solution at ordinary temperatures suffices to remove about one half of the emanation formed before it disintegrates, whereas from a nearly boiling solution almost all may be so removed. Since the period of half-change of the thorium emanation is approximately one minute, this means that, on the average, it takes about a minute for an atom of emanation formed in the cold liquid to leave it and enter the gaseous phase. The half period of actinium emanation being only 3.9 seconds, clearly it would be a very difficult matter to remove the emanation from an actinium preparation without leaving by far the greater part of it to decay *in situ*. On the other hand, in the case of the radium emanation, the half-period of which is some four days, it is easy, by passing a stream of gas through, or by exhausting the solution, to remove practically the whole.

In the case of thorium the best solid emanators are about equal to a solution at ordinary temperature. That is, some 50 % of the emanation produced may be removed from the solid unignited hydroxide or carbonate. Another method of removing the emanation, usually applicable only to radium preparations, is by fusion or strong ignition. In the case of radium chloride, the melting point is 954°, and at 920° there is a point of minimum emanating power which is associated with a point of polymorphic transformation. No doubt at sufficiently high temperature even infusible salts would be deprived of their emanation. In a recent method for the rapid estimation of radium, thorium, and actinium in minerals by the aid of their emanations, a fragment of the mineral is ignited in a cavity in a carbon rod maintained at dazzling temperature for a few seconds by an electric current.²⁶

The practical points to be noted are that if the emanation is wanted, the material is best kept as a solution, but if

the radioactive substance is required to retain its emanation in the open, then, in the case of radium, it is best to keep it as sulphate, and in the case of the other two radio-elements in the form of strongly ignited oxides. It is interesting to note that radium salts, precipitated along with the rare-earths as hydroxides or carbonates, have a very strong emanating power in the cold dry state.

The foregoing deals with the removal of the emanation from the radioactive preparation, for example by a current of air. From the air they can be readily and completely removed by condensation, by passing the gas through a U-tube at liquid air temperature.²⁷ To a very large extent they can be condensed also by cocoanut charcoal at ordinary temperature,²⁸ a method that might be useful if liquid air was not available, though it is not to be recommended otherwise.

The radium emanation, with its relatively long life, can be obtained by condensation in a fairly pure condition. The usual plan is to attach a mercury pump to a bulb containing the radium solution, and to pump off from time to time the emanation generated, along with the hydrogen and oxygen from the decomposition of the water. On explosion the emanation is left with the slight excess of hydrogen in very small volume. It may be handled by the methods described in detail in Travers' *Experimental Study of Gases* exactly as any other gas of the argon family. For complete purification it may be sparked with oxygen over caustic potash, or submitted to the action of vapour of calcium. Owing to its energetic chemical action it readily becomes impure again after purification, no doubt through its attacking traces of organic matter in the vessels employed. It is difficult to remove the last traces of carbon dioxide from its spectrum on this account.

The equilibrium quantity of emanation in one gram of radium (element) possesses a volume at normal temperature and pressure of only 0.6 cubic millimetre. In view of this extremely minute quantity the amount of information that has been accumulated on the physical constants of this new gas must be regarded as truly amazing.

Active Deposits.—The products of the emanations are in each case non-volatile at ordinary temperature, and have a relatively short period of life. They are collectively known

as the Active Deposits. The separation of the emanations mixed with air or other gases is, naturally, the first step in the separation of the active deposits, which, though in infinitesimal quantity, are capable of separation in the pure state, with the greatest ease. The successive products merely have to be separated from one another, not from, as is usually the case, an overwhelming preponderance of inactive matter. However short-lived, they can be simply separated in the pure state by physical methods alone.

Their collection and concentration on a metal surface or point is uniformly and simply effected by charging the surface in question negatively with respect to the surface of the containing vessel. It is probable that all products of disintegration, so formed and free to move in a gaseous atmosphere, possess initially, or acquire instantly, a positive charge. Even when the radiant particle expelled in the same disintegration is an α -particle, and is therefore positively charged, the charge of the product, or residue of the disintegrating atom, is always positive. The explanation of this apparent anomaly is, probably, that in the collision of the recoiling residue of the atom, after disintegration, with the gas molecules in their path a positive charge is acquired, that is, a negative electron is shaken out of the recoiling atom during the collision.

If it is desired to collect the active deposit from the thorium or actinium emanations, the latter may be passed by a current of air into a metal cylinder provided with a central electrode of wire along the axis held in place and insulated from the cylinder by rubber corks. The central electrode is attached to the negative pole and the outer cylinder to the positive pole of any source of potential, such, for example, as the electric light mains, a lamp being inserted in the circuit in case of an accidental short circuit. In most cases 50 volts, or even less, are ample for the purpose. To collect the radium active deposit, the emanation may be stored in a silvered glass flask, the internal coating of which is made positive, and a wire or knitting needle, sheathed in a glass tube to expose only the length required to be made active, and held in the flask by a rubber cork, is made negative.

The potential gradient, or volts per centimetre of dis-

tance, between the electrodes must be increased if the intensity of the radioactivity is very great. As a general rule it may be stated that the potential gradient required to concentrate the whole of the active deposit on the negative electrode is the same as would be necessary to produce "saturation" of the ionisation current through the gas under the same circumstances, that is, to collect all the ions in the gas at the electrodes.²⁹ Higher potential gradients than 50 volts per cm. are rarely necessary except in the case of intensely radioactive preparations, or where the concentration is to be effected on a very small area of surface.

Under these circumstances the active deposit is formed entirely on the negatively charged surface, which may be removed at any time from the emanation and studied by itself. Often the active deposit is then dissolved off in hydrochloric or nitric acid, or volatilised in whole or part by exposure to a high temperature, so that in such cases the negative electrode is preferably made of platinum.

Volatilisation Methods. Simple volatilisation at suitable temperatures often effects the removal of a radio-element from inactive material, or the separation of one radio-element from another. Many of the radio-elements, even when they exist only in infinitesimal quantity, are completely non-volatile, when heated in air, even at the temperature of the electric arc. Such, for example, are uranium X and radiothorium, both of which have the same chemical properties as thorium. But, like the latter, they may be distilled as chlorides from a carbonaceous mixture in a current of chlorine. As a general rule, the products in the series preceding the emanations are non-volatile when heated in air, whereas those following the emanations may all be volatilised at suitable temperature. Under ordinary circumstances polonium is one of the most volatile, and was separated by Mme. Curie from bismuth, which it resembles in chemical nature, by fractional volatilisation. Similarly the C members, which are chemically identical with bismuth, may be separated from the B members, which are chemically identical with lead, as they are much less volatile, when heated in air.

Latterly, the nature of the atmosphere in which volatilisation occurs has been found to exert a considerable influence. Thus in hydrogen, radium A, B, and C are all

volatilised completely at 650° , the volatilisation of radium C commencing at 360° ; whereas in air, no radium C is volatilised below 1200° , and none of the other two products below 700° .³⁰ In none of these cases does the quantity of the material investigated ever exceed the millionth of a milligram, but their behaviour is exactly what is to be expected of metals such as lead and bismuth, not only in the instance quoted, but in entirety.

It is frequently of importance to deposit the volatilised active material on a surface of given size and form, and suitable apparatus may be designed for doing this.³¹ With further reference to the volatilisation of polonium, it is interesting to note that the vapour condenses preferentially upon the palladium surface, and to a less extent on platinum, rather than on surfaces of other metals or quartz, porcelain, &c.³² This may be employed to effect the concentration of the material, and no doubt similar devices could be employed for other volatile radio-elements.

Recoil Methods.³³—To the special case of atoms disintegrating with the expulsion of α -rays, belongs what may be termed a "nascent" volatility, or volatility at the moment of formation, which is the effect of the recoil of the parent atom at the moment the α -particle is expelled. From the principle of the equality of momentum, since the parent atom is of the order of fifty times as massive as the α -particle, its velocity of recoil must be of the order of one-fiftieth of the velocity of the α -particle, that is, from 2.9×10^7 to 4.4×10^7 cm. per second. Such a velocity for a molecule of this mass corresponds with a temperature of between 1520 and 3300 million degrees Centigrade, and the nascent volatility exhibited is therefore not surprising.

If a carefully polished plate, on which is deposited an intensely active but unweighable film of, say, the active deposit of radium, is placed in a vacuum, the radium B atoms, formed in the α -ray change of radium A, and the radium D atoms, formed in the α -ray change of radium C, recoil from the plate and travel outward from it through the vacuum, being deposited on any surface placed in their path. The recoil particles carry a positive charge, and they will deposit preferentially upon a negatively charged surface. In this way they may be concentrated just as the active deposit

itself is concentrated, after its formation from the permanently gaseous emanation.

The recoiling particles have a certain very feeble penetrating power, about one-five-hundredth of that of the α -particle which accompanies their production. Thus the recoiling radium D atom from radium C has a "range" of 0.14 mm. of air at atmospheric pressure, or roughly 1 mm. in a vacuum of 100 cms. of mercury. They exhibit over this range many of the properties of α -particles, and strongly ionise the air in their path. In the case of the ultimate products, for example, that produced in the α -ray change of polonium, this ionisation of the recoiling particles of "radium G" is the sole experimental indication, as yet available, of the existence of this ultimate product, which, not disintegrating further, can no longer be detected once the change in which it is produced is over.

From what has been said, it will be obvious that, as the recoil atoms have only penetrating power sufficient to carry them through an excessively thin superimposed layer of material, the successful separation by recoil of the product of an α -ray change depends on obtaining the material as a uniform unweighable, or scarcely weighable, deposit on a very carefully polished surface. This is supported in a good vacuum opposite to the surface on which it is required to collect the recoiled product, the latter being connected to the negative and the polished plate, bearing the active film, with the positive pole of the electric mains. As in all such cases, it is advisable to operate in metal vessels or to cover insulating glass surfaces internally with tin-foil, and to connect all such surfaces, on which the deposit is not wanted, with the positive pole. Since the atoms recoil in every direction, only those recoiling in a direction away from the plate, obviously, can be separated, but under favourable conditions nearly the whole of the 50 % so recoiling from a plane surface may be separated. There is no perceptible recoil in β -ray changes, contrary to what was at one time supposed.

THE CHEMICAL CHARACTER OF THE RADIO-ELEMENTS

The Relation between Radio-Chemistry and Chemistry.—It has always been a matter for surprise, not to say scepticism, that it should be possible to investigate the chemical character of the evanescent products of radioactive changes, few of which are, or ever can be, studied in weighable or spectroscopically detectable quantities, and only one of which, radium, has been obtained pure in quantities sufficient for an ordinary atomic weight determination. Nevertheless the complete chemical character of the successive products has been steadily unravelled, and very simple and surprising general principles have been found to underlie the whole subject, which have notably enlarged our conceptions of elements in general.

Uppermost in the mind of any one approaching the subject from the point of view of chemistry is the question as to how far such knowledge as can be acquired of the chemical properties of these short-lived radio-elements can be accepted literally, and used as a basis of classification of the radio-elements in the same way as the common elements have been classified in the Periodic Law, for example. It may be urged that although an infinitesimal quantity of ionium, to take one case, behaves, when mixed with a relatively enormous excess of thorium, like the element thorium itself in all respects, the chemical nature of ionium, if it were possible to prepare it free from thorium, might be quite different.

The vague idea that infinitesimal amounts of radioactive matter may possess a chameleon-like nature, reflecting the properties of the substances with which they are mixed rather than their own, is not justified. The properties of the radio-elements, and with certain reservations with regard to adsorption, their behaviour under any defined set of conditions, is at least as definite as those of the common elements. The statement that ionium cannot be separated

from thorium, and many similar ones to be detailed in the sequel, is tantamount to saying that these radio-elements *can* be separated completely from all the other elements differing in chemical reactions from the one specified. Admittedly many have not, and, probably, never will be separated from the element they most resemble. But it is inconceivable that a radio-element when pure might possess chemical properties, allied most closely to those of, say, lanthanum, and be capable of being separated from lanthanum but not from, say, thorium out of a mixture containing both of these elements.

In the first place, we must define more clearly the term "pure" in connection with the radio-element. First, there is the usual sense conveyed by the words "chemically pure," denoting an ideal rather than an attainable condition, be it with radio-elements or any other, a sense that may be rightly used, possibly, for radium preparations, such as those on which atomic weight estimations have been made. Secondly, there is the sense of "radioactively" pure, meaning that the substance is free from all other radioactive substances, though mixed with a possibly minute, but nevertheless overwhelming absolute preponderance of inactive matter. Lastly, there is another and very important sense, which may conveniently be termed "radio-chemically" pure, in which the radio-element, though mixed, possibly, with any quantity of inactive matter of totally different chemical nature to act as a vehicle for its transport, is yet free from substances chemically analogous to, or identical with itself. Such is frequently the condition of short-lived products repeatedly separated from their pure parents, and of those prepared as active deposits or by recoil and analogous methods.

As the methods of detection and measurement are based wholly on radioactive phenomena, the presence of inactive matter does not necessarily interfere apart from secondary considerations involved in the absorption of the rays therein and the weakening of the activity on that account. A simple example will perhaps make this clearer. The properties of the radium emanation by which it is studied are not shown by any common gas, and it is a matter of indifference with what gas it may be mixed. By passing it through various absorbents, in each case in presence of sufficient of another gas, not absorbed by the reagent, to serve as a vehicle to transport it, it is a simple matter to

prove that the emanation is not absorbed by any known reagent, and that it is, therefore, a new member of the argon family of gases occupying the zero group of the Periodic Table. To thus characterise the chemistry of the radium emanation, a quantity millions of times less than would be visible as a bubble, or could be spectroscopically detected, or weighed on the micro-balance, did actually, as a matter of historical fact, suffice in 1902.⁶ Though, since then, enormously larger quantities have been available, and it has been worked with in a state of approximate purity, nothing has been added in consequence to our knowledge of the chemical properties of this radio-element. The example is, of course, a negative one, as it were, because it concerns the absence of all chemical properties in this particular case, but it will perhaps serve as a step towards the understanding of how it is that the absolute minuteness of the quantities involved are not in themselves a barrier to the study of the chemistry of the radio-elements.

In the next step, let us neglect any inactive matter present and concentrate our attention on the case of separating two chemically different radio-elements from one another. Such separations are effected as completely and simply as ordinary chemical analysis, always provided that, if such a mechanical operation as filtration is involved, there must always be sufficient quantity of matter to form a filterable precipitate. Under such conditions it is always found, for example, that polonium is completely precipitated in acid solution by sulphuretted hydrogen. Ionium is not so precipitated, but is by ammonia, whilst radium is precipitated by neither reagent, but is completely by sulphuric acid. So that, in presence of precipitable quantities of any of the members of these three analytical groups, the complete separation of these three radio-elements, chosen as examples, from one another is as easy with absolutely unweighable quantities as ordinary analysis. Going further, it is equally possible to show that polonium resembles bismuth more nearly than any other of the metals of Group II, but does not resemble it absolutely, and is in fact a new type of chemical element, though it has never yet been obtained in quantity sufficient to be worked with, apart from inactive material to serve as a vehicle for its transport. Similarly, radium resembles barium more nearly than it

does any other of the metals of Group IV, but does not resemble it absolutely, and is, in fact, another new type of chemical element. It is fortunate, but not essential to this conclusion, that in this one case sufficient radium can be got to be weighable and visible by itself as a new chemical element, and almost as full information can be obtained for it as for the inactive elements.

Lastly, ionium not only resembles thorium more nearly than any other member of Group III, but is found to be chemically identical in properties with it. Ionium, in presence of sufficient thorium to act as a vehicle, may in quantities, however infinitesimal, be completely and simply separated from any mixture containing any or every known element, by the simple device of separating the thorium therefrom by known methods. Ionium is a new *radio-element*, but is not a new *chemical* type of element. This is a new conception. In every detail of its radioactive properties, the velocity or range of its α -rays, its period of change, the character of its product and of its parent, ionium is distinct and different from every other radio-element. But in its chemical nature it is not new. On account of its identity in this respect with the element thorium, every detail of its chemical nature is known "by proxy" as completely as though it were obtainable, like thorium, by the ton. Ionium cannot be obtained "radio-chemically pure" on account of its long period and the presence of thorium in all minerals from which it may be obtained. This is in contrast to many of the radio-elements, similar to ionium in not being chemically new, for they can usually be "grown," often *via* the gaseous emanation, in a condition of complete radio-chemical purity.

Before pursuing this remarkable new line of development, let us push the question of chemical separations a little further to such operations as do not involve mechanical processes like filtration. Volatilisation is such a case, already considered. The extraction of one liquid by another is one not yet considered. Extract a uranyl nitrate solution with ether, for example, and it will be found that the uranium can be extracted from the aqueous solution completely by a sufficient number of extractions, but this uranium, so extracted, gives only α -rays, whereas the β -rays of the original uranium come from a constituent, really a product, called

uranium X, which remains in the aqueous layer completely. Now if such a thing as pure uranium nitrate or pure ether were practical, rather than ideal existences, then it would be easy to evaporate away the ether and obtain this β -ray product of uranium, which is quite non-volatile, in the pure state. But, unfortunately, however "pure" the materials used might be, the impurities so extracted would probably outweigh a millionfold the uranium X so obtained, of which, in a ton of uranium, it may be calculated these never can exist much more than one-hundredth of a milligram. A very insignificant part of such a quantity would make an X-ray screen in the dark visible to a thousand people in a large hall, even though it were mixed with millions of times its own weight of foreign impurities.

But if, relying on such *radioactive* evidence and neglecting such unavoidable impurities, we study the chemical nature of uranium X, again we reach a surprising conclusion. In chemical nature it also is *identical* with thorium and with nothing else. In radioactive nature it is unique, and as different from ionium, on the one hand, giving β - and not α -rays, being short-lived instead of long-lived, and so on, as it is from thorium on the other. But in chemical character it is not unique. Differing recognisably from every other known element, it yet resembles one with such undeviating fidelity that processes which are capable of removing from it every other known element always leave the concentration of the substance relatively to this one element unchanged.

The Position of the Radio-Elements in the Periodic Table.

—Thus in the broadest way the results of the purely chemical study of the radio-elements lead to the distinguishing of two classes—a first class, which are new only on the radioactive side, but which on the chemical side are already completely known and familiar; and a second class which, in addition to possessing a characteristic and distinctive radioactivity, are also new in chemical properties—that is to say, they are new types of chemical elements. In other words, we have those which are new only in the fact and manner of their demise, but during their existence are indistinguishable from well-known elements, and we have those which, in their normal life as well as sudden death, are unique in behaviour and distinct from every kind of element previously known.

The first class, naturally, are the less interesting but the easier to work chemically with. The second class combine with all the charm of the unknown in chemical behaviour the added elusiveness of rarely, if ever, being present in weighable quantity. Hence the complete elucidation of their chemistry presents a beautiful new problem, which it need hardly be said is very far from worked out. But we must now combine with the chemical knowledge of the products the study of the actual processes of disintegration, accompanied as it is with the expulsion of α -particles, or helium atoms carrying two positive charges, and β -particles or negative electrons.

The disintegration series affords a most remarkable picture of the actual process of the production of the elements from one another, of which the Periodic Law is, as it were, the consequence. Just as from an instantaneous photograph of a waterfall the movement of the apparently motionless water can be inferred, so from the Periodic Law the continuous transformation of the apparently unchangeable elements has been suspected. Radioactivity has, as it were, cinematographed these transformations, with the result to-day, which none ten years ago could have dared to imagine possible, that in three separate instances we are tracing the successive transit of matter from group to group of the Periodic Table.

As was originally pointed out in the first edition of this book, the expulsion of the α -particle causes a change in the position of the radio-element in the Periodic Law by two places, in the direction of diminishing mass, that is, from right to left in the Table as usually represented. Since then, the increase in our knowledge of the successive products in the disintegration series, of their order of sequence, and of their chemical character,³⁴ has resulted in a complete generalisation being established connecting the position of the radio-element in the Periodic Table, and the nature of the change in which it is produced. This generalisation, more or less independently arrived at by A. S. Russell, K. Fajans, and the author,³⁵ has been dealt with in Part II of this book, and its theoretical significance detailed. In this Part it will only be necessary briefly to state the nature of the generalisation, and to point out its vital importance in the practical problems that arise in the chemical separation of the radio-elements.

The expulsion of the α -particle causes a shift of position of the radio-element by two places from right to left, the expulsion of the β -particle a shift of position of one place from left to right. The passage, of the atoms successively produced, through the Periodic Table is thus not straightforward, but alternates backwards and forwards. Owing to the α -ray changes being far more numerous than the β -ray changes, there is a general nett movement in the direction from right to left, extending over the last twelve places of the Periodic Table from uranium to thallium. This is shown in Fig. 3 at the end of the volume.

The first class of radio-elements, already referred to, the chemistry of which is completely known by proxy, are all chemically identical with one or other of the last five members of the Periodic Table, as it would be found represented in text-books prior to the discovery of radioactivity—namely, uranium, thorium, bismuth, lead, and thallium. The members of the second class, of new types of chemical elements, are all, also, identical with one or other of five new elements—namely, in order of their discovery, radium, polonium, actinium, the emanations, and “eka-tantalum.” These five new elements correspond in character with what is to be expected of the hitherto missing heavier analogues of barium, tellurium, lanthanum, xenon, and tantalum respectively.

Just as in the first class, more than one of the radio-elements have been found identical with each of the five previously known elements—thus there are, in each case, four identical with thorium, bismuth, and lead respectively—so it is with the second class. There are three emanations, for example, alike, negatively rather than positively, in their complete absence of chemical properties. Chemically identical with radium are three other radio-elements, of which mesothorium I is the longest-lived and most important. For these two the chemistry may be considered as perfectly known, as that of all the members of Class I. There remain three—actinium, polonium, and eka-tantalum—of which no stable representatives are yet known. The unsolved problems in connection with the chemistry of the radio-elements have thus narrowed themselves down to the elucidation of the properties of these three still incompletely known types.

Actinium, the homologue of lanthanum, resembles that

element and the other rare-earths very closely, though there are probable differences. The difficulty is that actinium, being a minor branch product, is a very scarce and difficult substance to obtain, even for a radio-element. Knowledge of its chemistry is rather backward on that account. The sole known representative of the homologue of tantalum, which is known also by the names of uranium X_2 or brevium, has a period of average life of only some two minutes, and hence not much detailed knowledge of its properties can be expected unless a more stable representative is found. Such an one (called uranium Z in Fig. 2) in all probability does exist, but has not yet been obtained. There remains polonium, and, as the homologue of tellurium, standing in the Periodic Table next to bismuth, its chemistry promises to be extremely interesting. But the relatively short life and consequent minuteness of the quantities available mitigate against any complete chemical knowledge in the ordinary sense being obtained. Not that a great deal is not known, but much of it is not directly comparable with other chemical knowledge, and belongs to an order of concentration not directly investigable except by radioactive methods.

The result, therefore, of this brief survey of the subject is to show that, apart from the three last examples considered, the chemistry of the whole of the radio-elements may now be considered to be known with singular completeness, and the somewhat gloomy prognostications of the hopelessness of attempting to investigate such infinitesimal quantities of evanescent materials have been strangely falsified.

But not only has the chemistry of the radio-elements been cleared up in the most wonderful way by this generalisation. We are face to face with something that is new and vital in the nature of the elements in general. This aspect is discussed more closely in Part II.

The new conception that different radio-elements with different atomic weights, derived from different parents and yielding different products, may yet be absolutely identical in chemical properties, receives a ready explanation from Fig. 3. Chemical tests would only distinguish between ten kinds of radio-elements, but the radioactive evidence shows that there are thirty-four. The separate places in the Periodic Table thus do not correspond with single elements, necessarily, but with single chemical types of elements. All the

elements in the same place exhibit identical chemical properties. For this reason these are called "isotopes." Ionium, thorium, radiothorium, and uranium X are isotopes, mesothorium I is isotopic with radium, radio-lead with lead, and so on. It is probable that it is the nett internal positive charge of the nucleus of the atom, and not its mass, which conditions its chemical properties. The expulsion of one α - and two β -particles from the nucleus leaves this charge and the chemical properties the same as originally, though the mass is reduced by four units by these changes. The successive "places" in the Periodic Table correspond with unit differences in the nett charge of the atomic nucleus, and the identity of this charge is all that is implied by chemical proofs of homogeneity. This charge changing unit by unit gives us the Periodic Table of elements. In Fig. 3 the magnitude of this positive nuclear charge, which is called the atomic number, is indicated at the bottom of the diagram. Uranium is the last and heaviest of ninety-four possible elements. The real complexity of matter, now that isotopes have been shown to exist among the radio-elements, may be far greater than the chemist's table of the elements indicates. The possibility is not excluded that some common elements may be isotopic mixtures.

In contradistinction to the unit negative charge, or electron, which is so nearly massless, the positive charge is invariably associated with a mass of atomic magnitude and may be such a mass. It is not impossible even that its mass may be to the first approximation constant, and the same as that in the case of the α -particle, namely, two units of mass per one unit of positive charge, though hydrogen with mass 1 and atomic number 1 is an exception. For all the other elements, the atomic mass is either equal to or greater than twice the atomic number, and as the atomic mass increases, it increases faster than twice the atomic number. We have evidence that negative electrons, as well as positive charges, enter into the constitution of the heaviest elements, because they are expelled therefrom as β -rays. Uranium so expels six electrons in its charges. The atomic mass of uranium—238—corresponds with between 119 and 120 positive charges on the simple idea being considered. Its atomic number or nett nuclear positive charge being 92, it would be necessary to suppose that the nucleus contains 27 or 28

negative electrons in its constitution. Whether or not such simple ideas may help to solve the problem of the true significance of atomic weights it is, however, too early yet to state.

Practical Consequences of the Existence of Isotopes.—

✓In dealing with very large quantities of minerals of complex composition, in which the only safe plan is to assume that probably one-half, at least, and possibly all the known elements are present in concentration greater than that of the radio-element it is desired to separate, it is necessary to concentrate by successive stages. At some stage it is usual to add an element, if not already present in sufficient quantity, either chemically similar to or isotopic with that which it is desired to separate. As an example of the first case, in the manufacture of radium, the addition of barium to the reagents before use, to remove sulphates and to ensure a convenient quantity of concentrate, capable of being handled without proportionately large loss, is a common practice. So also in analysis, the addition of a member of the same group as the radio-element is often a very useful preliminary to its complete separation, first with and then from the added substance. But when the element added is isotopic with that being separated, though the addition may enormously simplify the separation and enable a complete separation to be carried out, it can never be removed again. The device then entirely prevents the radio-element from being prepared in a radio-chemically pure form. Thus Boltwood in his work on ionium adopted the device of adding thorium repeatedly and separating it, to insure the complete removal of the ionium from the mineral, which was the object of the work rather than the preparation of the ionium in concentrated form.³⁶ × On the other hand Welsbach, in his work on the rare-earth fraction of thirty tons of Joachimsthal pitch-blende, purposely added nothing analogous to the radio-elements therein.³⁷ However, there was sufficient lanthanum and thorium present in the original mineral to preclude the actinium and thorium being separated in the radio-chemically pure state. Nevertheless, the amount of thorium present was so small that the final ionium preparation weighed only a few grams, and, there is little doubt, must have contained a considerable percentage of its more radioactive twin brother ionium.

Considerations such as those just considered underlie and limit the possible extraction of the technically important radio-elements in minerals. In the uranium minerals, radium and polonium, being new chemical elements, of which no stable representatives exist, are readily obtained in a concentrated form. If the first only has so far been obtained in the pure state, there is at least no known theoretical reason why ultimately the latter and also actinium should not also be so obtained. In accordance with the principles already stated, they are separated first with and then from the barium, bismuth, and lanthanum in the mineral. The attempts so to separate the predicted long-lived homologue of tantalum have so far failed, owing, doubtless, to the extreme variability and uncertainty of the chemical properties of tantalum, and possibly to the resemblance not being sufficiently close to serve the purpose.³⁸

But there is no possibility of obtaining radio-lead (radium D) from minerals in concentrated form, because it is isotopic with lead, and there is always a considerable amount of lead in such minerals. In consequence, this product is technically of very little use, though if it could be concentrated it would be as valuable as the others. As lead is believed to be the end product of the disintegration, it would seem to be definitely impossible ever to extract the radio-lead from uranium minerals in a concentrated form. The only way of preparing radio-chemically pure radio-lead is to grow it. The emanation of radium must be pumped off as it forms, and left to undergo its rapid changes in sealed vessels. The radium D or radio-lead, in course of time, then accumulates on the walls. Using considerable fractions of a gram of pure radium, the quantity of radio-lead so accumulated may, if capillary tubes are employed to contain the emanation, come within the region of visibility as a submetallic deposit. Ordinarily, however, it is quite invisible, though its radioactivity may be very great. The radio-lead, separated from pitch-blende with the whole of the contained lead, although but feebly radioactive, is not entirely useless, because it is a valuable source of polonium. The polonium that accumulates in it as time elapses may readily be separated from the lead and got in concentrated form. But, of course, the somewhat short life of polonium militates against its usefulness, and the newer radio-element, ionium.

is, on account of its permanence, to be preferred for almost all purposes for which polonium at one time was used.

The case of ionium has already been considered. Clearly the limit of concentration is set by the quantity of thorium in the mineral. It is very fortunate that many of the secondary uraninites contain such minute amounts of thorium, not so much on account of the ionium, but for another reason that will shortly be clear. This exhausts the list for the uranium minerals. Short-lived elements like uranium X are, of course, always grown from the pure parent, which, after purification from any especially objectionable impurities, is simply left to reaccumulate the product, which is then separated. As that separated decays, another quantity reforms, and the separation must be repeated as often as, or for as long as, a supply of the evanescent material is required.

In the case of the thorium minerals, matters are more complicated. Though uranium minerals are known, like the secondary uraninites or pitch-blendes, which are practically free from thorium, the converse is not true. All thorium minerals seem to contain uranium, the lowest ratio between the elements being that for Ceylon thorite, which contains some 60 % of thorium and from 1 or 2 % of uranium. Hence all thorium minerals contain all the known radio-elements to greater or less degree. In Ceylon thorianite, where the thorium is present in from three to six times the quantity of uranium, the radioactivity of the products of the two series is of about the same order, owing to the rate of change of uranium being more rapid than that of thorium.

Considering first a pure thorium mineral, to which Ceylon thorite nearly approaches, and assuming, what is never the case, that uranium is completely absent, the long-lived and technically important constituents are mesothorium 1 and radiothorium. Neither is a new chemical type, the first being isotopic with radium and the second with thorium. Mesothorium is readily separated, like radium, by the addition of barium, if necessary, but the separation of radiothorium is, and will probably for ever be, impossible. Like radio-lead in the uranium series, the only way of obtaining it in concentrated form is to grow it from its pure parent mesothorium, after the latter has first been separated from the thorium mineral. The whole of the radiothorium in the mineral

originally—and this is responsible for by far the greater part of the total activity—is thus useless. The period of average life of radiothorium is about three years. In effect, one loses three years' production of radiothorium however well the chemical operation may be planned and carried out. But the further consideration of this somewhat complicated case may be reserved until the thorium products are considered more in detail.

Lastly, let the mineral contain both uranium and thorium, and such minerals are very numerous and important. The period of thorium being three or four times as long as that of uranium, in a mineral with three or four times as much thorium as uranium, the thorium series of products will be of similar order of activity to the uranium series of products. Mesothorium, being isotopic with radium, is necessarily separated with the latter. Hence pure radium can only be prepared from a pure uranium mineral. All radium prepared from mixed minerals is necessarily contaminated to greater or less extent with mesothorium. As the activity of pure radium is the usual standard in which radioactive measurements with concentrated preparations are expressed, and as mesothorium has the comparatively short period of average life of eight years and its activity is a complicated function of the time, the origin of the radium to be used as standards of measurement is thus of vital importance. As already remarked, it is fortunate that so many of the technically useful uranium minerals are practically free from thorium.

All the ionium and radiothorium in thorium minerals will remain with the thorium, and cannot be concentrated therefrom whatever chemical processes be employed. Hence all thorium preparations necessarily contain some ionium, and if prepared from common thorium minerals, this radioactive impurity may be very important. It would be possible to cite numerous instances from the literature where failure to appreciate these fundamental considerations had involved possibilities of error.

Since ionium is the parent of radium, all thorium preparations, however carefully they may be purified from this element, will grow radium in the course of time, withal in minute, though not, in special cases, necessarily unimportant, quantity.

Radioactive analysis recognises some thirty-four radio-elements, whereas chemical analysis, of these thirty-four, only distinguishes ten. Hence by chemical analysis of a mixed uranium-thorium mineral only ten groups of radio-elements are able to be separated. But by coupling chemical analysis with the lapse of time, the analysis may be pushed further. As a single example—Is the radium separated from a mineral pure or does it contain also mesothorium? Some time after the separation a trace of a Group III element, such as aluminium, added to the radium and precipitated by ammonia, will bring down the regenerated radiothorium, if mesothorium is present, and not if it is absent. Radiothorium may be distinguished very sharply by its power—again after lapse of time—to produce the characteristic thorium emanation. It may be remarked that this test is so delicate that it will detect the mesothorium in radium prepared from Joachimsthal pitch-blende. That is to say, it will reveal the thorium present in this mineral, although it is less, probably, than one gram per ton of uranium.

In the foregoing section the main consequences of the existence of isotopes in the separation of radioactive minerals have been discussed purely from the practical point of view. We have learned that radio-lead and radiothorium cannot be separated from the original constituents of the mineral, but that, first, their parents must be separated, and then, from these parents after the products have accumulated, separation by chemical means is possible. This, the universal method of obtaining short-lived products, is in these cases tedious and time-consuming by reason of the comparatively long life of the products being grown. Also, that radium and thorium are very liable to contain mesothorium and ionium respectively, in addition to their own products, in which case no process of chemical purification is of the slightest avail. The only way is to start in the first place from suitable minerals, thorium-free uranium and uranium-free thorium minerals, respectively. But these are the only important cases. The wonder is, rather, that the chemical identity of so many of the products with one another and with common elements interferes so little with their separation by chemical methods.

ADSORPTION, ELECTRO- AND COLLOIDO-CHEMISTRY OF RADIO-ELEMENTS

Adsorption.—The separation of the radio-elements in minute amount from solutions by means of adsorbents, notably, barium sulphate and charcoal, played at first some part in the practical methods employed, but, with the better elucidation of the chemical properties, such methods are now less frequently employed than formerly. The action of barium sulphate in separating, for example, uranium X and other isotopes of thorium, must be distinguished from its normal chemical action in separating radium and its isotopes. As is well known, barium sulphate has the property of adsorbing many substances, notably iron and the rare earths, when precipitated in their solution, and the adsorption of the isotopes of thorium and actinium is analogous. A curious point in the adsorption of uranium X by barium sulphate is that, in the absence of thorium, the uranium X adsorbed is not dissolved by treatment with acid, whilst in the presence of thorium the uranium X and thorium, which are both adsorbed in the same ratio, as is to be expected of isotopes, may be redissolved from the precipitate by acids. Zirconium has no influence, but cerium prevents the complete adsorption, and in this case the uranium X adsorbed cannot be redissolved by acids from the barium sulphate.³⁴ Metasilicic acid gel has been claimed as an adsorbent for radioactive substances,³⁹ but experiments made in the author's laboratory did not confirm this. It is a matter of common knowledge how little the silica, separating from solutions of radioactive minerals in acid on evaporating to dryness, adsorbs the radio-elements present.

The phenomenon of adsorption at the surfaces of solids is probably a general property of all surfaces, which varies enormously both with the nature of the surface and the

nature of the substance adsorbed. In the analytical reactions of the common elements it is only remarked when the adsorbing surface can take up weighable quantities of the adsorbed materials—quantities, that is, which correspond to more than 10^{18} molecules. A given quantity of an adsorbent might be able, for example, to adsorb a million molecules of most substances, and more than 10^{18} molecules of one particular substance or molecular species. It would then be regarded as an adsorbent of the one substance alone. In a solution containing a radio-element the adsorbent might adsorb the radioactive substance, if present in quantity below a million molecules, completely, provided only that no other chemically similar substance was present. But if the radio-element were physically and chemically indistinguishable from some common element, which was present in great excess, though, possibly, still far less than weighable quantity, the adsorption of the radio-element might be practically completely prevented.

Owing to adsorption those radio-elements, with chemical and physical nature indistinguishable from a common element always present with them in the natural minerals, will behave definitely, whereas those others which are not allied to any known common element in properties will probably behave the more indefinitely the shorter their period of life, and the more they depart in chemical character from any impurities that may be present.

Thus in these respects the properties of radio-lead and polonium, separated directly from minerals, are likely to be very different from those of the radio-chemically pure substances grown from the emanation.

Another example is the prevention of the adsorption of uranium X by a trace of thorium.⁴⁰ On the view put forward, provided that the added isotope is not adsorbed, its addition must completely prevent the adsorption, as it has been shown to do in this case. Clearly this suggests a test as to whether a radio-element is the isotope of a common element. For if the radio-element continued to be adsorbed without the isotope, a separation would thus be effected and the two substances could no longer be regarded as non-separable. There is, however, no example of this, though specific cases have been examined. Not

as much work as is desirable, however, has yet been done on this point.

Later work has shown, both, that other substances than thorium, such as zirconium and even benzoic acid, have a similar inhibiting effect on the adsorption of uranium X, and also that thorium prevents the adsorption by charcoal of other substances than uranium X, for example, copper.⁴¹ This is of great interest from the point of view of the nature of adsorption, but there is nothing unfavourable in it, as has been alleged, to the existence of isotopes. The important point is that thorium does inhibit the adsorption of uranium X, and no case is yet known of an adsorption process altering the ratio between a radio-element and an inactive isotope.

Electro-Chemistry.—Many of the radio-elements, particularly those following in the series after the emanations, are readily deposited from solution on immersed metals. Thus polonium is one of the most "noble" or readily deposited, and may be deposited on platinum, bismuth, or copper, and even (in the radio-chemically pure state) on glass to a considerable extent. If a separation from other easily deposited radio-elements is desired, bismuth is to be recommended. The C members, which are isotopes of bismuth, are more noble or readily deposited by metals than the B members, which are isotopes of lead, and nickel, in sheet or finely divided form, is much used to separate these two successive products. Its specific behaviour in this respect, depositing the C member nearly completely, is rather remarkable. Thorium D and actinium D, the isotopes of thallium, are less easily deposited than the B members.

Before the latter fact was known, von Lerch put forward as a general rule, which is known by his name, that the successive products in a disintegration series are progressively more noble in their electro-chemical behaviour. This is true of the B and C members and of radium F, which were the members first studied. A glance at Fig. 3 will show that to the left of the emanation group the successive places in the Periodic Table represent a continuous decrease in electro-chemical nobility, in order thus: (1) polonium or radium F, and its isotope radium A; (2) bismuth and its isotopes, the C members and radium E; (3) lead and its

isotopes, the B members and radium D ; (4) thallium and the isotopic D members. To the right of the emanation group, the members are never deposited on immersed metals. In electrolysis, radium and its isotopes, like barium, may be to some extent deposited on a mercury cathode, or on other electrodes in alkaline solution.⁴² Actinium and its isotope mesothorium 2 may be electrolytically deposited from a boiling, nearly alkaline, solution on a silver cathode.⁴³ The same method has been recently employed to separate and obtain in the form of a good coherent deposit radio-thorium from its parent mesothorium 1.⁴⁴ But with these isolated exceptions, electrolytic deposition is usually confined to the post-emanation members.

The chemical identity of isotopes has been fully confirmed, and extended by the study of their electro-chemical behaviour.⁴⁵ Further, in this field, as the researches of von Hevesy have recently shown, the possibility of obtaining the materials experimented upon in the radio-chemically pure condition, in absolutely infinitesimal but yet easily determinable concentration, has resulted in advances of much interest in the science of electro-chemistry itself.⁴⁶ In the first place, dealing with ordinary substances, before a detectable amount of a metal is deposited on the cathode, a certain potential difference, known as the decomposition voltage, must be exceeded. But with radioactive methods the deposition can be detected even with such infinitesimal quantities as, according to theory, must be deposited by *any* difference of potential, and the decomposition potential need not be attained before notable deposition occurs. This leads us to expect that every metal is capable of causing the deposition of every radio-element to greater or less, but always detectable, degree, and, in neutral solutions, this has been found to be the case for a large number of the radio-elements and many metals, not excepting even the noble metals.

Again, in dealing with these infinitesimal concentrations, even insulators, like glass, can act as a metal and deposit a perceptible amount of a radio-element. There is, probably, a potential difference between glass and the solution in which it is immersed which can be detected and studied by this deposition of radio-elements, though not by the

ordinary electro-chemical methods. This is one of the dangers in working with radio-chemically pure polonium. Extreme precautions are necessary to avoid its loss by deposition on the walls of the containing vessels. It may be redissolved by strong acids, but on dilution it is again deposited.

The mental picture one forms of the deposition of copper on the cathode, for example, by electrolysis of a copper solution, is very far from correctly representing the deposition of a radio-element. In the first case the electricity transported to the cathode is carried entirely by the copper ions, whereas in the deposition, for example, of radium B and C on the cathode by electrolysis of the solution, the quantity of radium B and C ions present is insufficient to convey an appreciable current. It is necessary, rather, to neglect almost entirely the transport of electricity, or the electric current as such, and the total voltage between the cathode and anode, and to confine attention solely to the single electrode potential between the depositing metal and the solution. Without current flowing, every metal immersed in a solution containing its own ions takes up a definite potential difference, and, according to the magnitude of this P.D., will deposit any radio-element in solution to greater or less degree, without an anode or without any electric current flowing. But, when a current flows, this natural P.D. is more or less modified. In the case of a noble metal such as is frequently used for a cathode, the natural potential the metal takes up is positive to the solution, but when a current flows from an anode to this cathode its effect is to diminish, and, if strong enough, to reverse this natural potential difference, increasing the amount of the radio-element deposited. It is by such considerations as these, rather than on ordinary electrolytic lines, that the behaviour of radio-elements in the radio-chemically pure condition on electrolysis is regulated. Polarisation of the anode, again, by the passage of a heavy current, may by its effects on the single potential difference cause a radio-element, like polonium, to be deposited on the anode as well as on the cathode.

Let us now consider a solution of either of the three active deposits in dilute acids. Such a solution after the

disappearance of the short-lived A member is practically a mixture of the B and C members. Now immerse in such a solution a suitable electrode, and, as may be done practically in a variety of ways, pass from a strongly electro-positive P.D., such as is given by a noble metal, to a strongly electro-negative P.D., such as is given by easily soluble metals like zinc or magnesium. At first the deposit on the electrode will be practically the pure C member, but as it becomes more and more electro-negative, more and more of the B member will accompany it. At a potential of 0.6 volt, measured against the calomel electrode, the two members are deposited in equilibrium proportion.

The Radio-Elements as "Indicators."—Now the ratio of the B to C member in the deposit is readily deduced from the form of the decay curve of the α -rays from the deposit obtained. The radiation from pure C would decay exponentially and relatively rapidly with the time. That from pure B would first increase owing to the growth of C and then decay more slowly. From the form of the curve the initial ratio between the two members may be deduced. Hence, from a knowledge of the P.D. corresponding with any given proportion between the B and C member deposited, the P.D. itself may be determined if the proportion of the two members in the deposit is found. In this way the radio-elements may be used as indicators in determining single potential differences not otherwise experimentally determinable.

Thus, on the Nernst theory of the origin of E.M.F., every metal immersed in absolutely pure water should be negative to the water until some of the metal, not necessarily an analytically detectable quantity, has dissolved as ions. Thus copper at the first moment of its immersion in a copper-free solution should behave as a strongly electro-negative metal like zinc. After an immersion for 0.2 second, of a copper electrode in a solution of the active deposit, the ratio of the B and C members deposited showed that the potential of the copper to the solution was —2 V., with reference to the calomel electrode. Thus the use of the radio-elements as indicators in electro-chemistry has already produced interesting and welcome confirmation of the existing theory, and the field opened out is a very wide one.

Quite in accord with the inhibition of the adsorption of a radio-element, is the prevention of the electro-deposition by an inactive isotope.⁴⁵ Thus, if by suitable adjustment of the potential difference, it is desired to deposit pure thorium C from the solution of the active deposit, the addition of lead, the isotope of the B member, in appreciable quantity is advantageous. In presence of lead, the deposition of thorium B is appreciable only at 0.44 V., whereas in the radio-chemically pure condition perceptible deposition occurs at 0.33 V. In presence of bismuth, the C member is deposited at a potential of 0.08 V., and a bismuth plate immersed in the solution showed the same potential. A very interesting detail about thorium B is that, exactly like lead, it is deposited on the anode as peroxide at a potential between 1.0 and 1.1 V. Good use of this behaviour of lead has been made in the separation of polonium from radio-lead extracted from minerals. Enough concentrated nitric acid is added to the lead nitrate solution to prevent the cathodic deposition of lead. Under these conditions most of the polonium can still be deposited at the cathode, along with radium E, which, however, quickly decays.

So far as it has yet been possible to examine them, the radio-elements isotopic with lead and bismuth show, in presence of these elements, an identical electro-chemical behaviour ; whereas by studying them in the radio-chemically pure condition, it has been possible to examine, by proxy, the electro-chemical properties of lead and bismuth at potentials both above and below the decomposition voltage—over a range, that is, which otherwise could not be studied.

But it is not only in electro-chemical work that the radio-elements may be made to give, by proxy, information about common elements. The solubility of the most insoluble compounds of lead, the chromate and sulphide, have been directly determined by experiments with the isotopic radium D as indicator.⁴⁷ If a sufficient quantity of the latter is mixed with the lead compound, the small part dissolved will have a detectable activity, from which its quantity may be deduced, although too small to be estimated analytically. In this way it has been found that the solubility of lead

chromate at 25° is 1.2×10^{-6} grams per litre, and of lead sulphide 3×10^{-4} in water, and 1.5×10^{-4} in presence of excess of hydrogen sulphide. Many other examples suggest themselves in which ionium or uranium X might be used as indicators for thorium, radium E for bismuth, and so on.

Existence of Colloidal Solutions of the Radio-Elements.—Although, in sufficiently concentrated acid solution, it is probable that the radio-elements exist as positive ions, and their transport to the cathode during the passage of a current is analogous to ordinary electrolysis, with the differences already alluded to, the researches of Godlewski and Paneth have shown that frequently the radio-elements exist as colloidal rather than ionic solutions, and their electrochemical transport is allied to electrophoresis rather than electrolysis.⁴⁸

To take first a very striking and simple case. Polonium (radium F) may be separated from radium D and E by dialysis of a nearly neutral solution of the radio-lead nitrate through animal membranes or thin parchment paper. The lead, radium D and E, pass through as crystalloids, but the polonium remains behind in the cell in a pure condition.

Further work showed that in neutral solution the velocity of dialysis of radium E, and in an ammoniacal solution of thorium B, may be much reduced. In general, according to the degree of acidity, both hydrosols and ions of the same radio-element may exist together in the solution. The change from crystalloid to colloid is accompanied by a change of sign of the electric charge, and the colloid particles migrate in an electric field to the anode instead of to the cathode. If a parchment membrane is inserted in such a solution containing both forms, the cathode deposition is not prevented but only hindered, whereas the anodic deposition is completely suppressed.

Much work has also been done on the radium active deposit formed in pure water containing dissolved emanation. Under these circumstances all the products, radium A, B, and C are present as hydrosols, but the A member is deposited on the anode, the B member on the cathode, and the C member on both electrodes. In other words, the A member exists as a negative hydrosol, the B member as a positive hydrosol, and the C member as

a mixture of both varieties. It has been suggested that the radium A starts with a negative charge as a negative hydrosol. In its α -ray change the radium B atom produced is expelled by recoil from the colloidal aggregate and forms a negative hydrosol, but in the β -ray change of radium B the radium C atom is not expelled. According as the colloidal aggregate contains excess of radium B atoms or radium C atoms, it is negative or positive, and migrates accordingly. As time goes on, and the majority of the B atoms are transformed into C atoms, the sign of the charge on the colloidal aggregate changes from negative to positive.

On these solutions many of the consequences of the general theory of colloids have been tested and found to hold good. Negative colloids, such as arsenious sulphide and platinol, neutralise the positive hydrosols present and reserve their sign, so that in their presence cathode deposition is prevented, and all the products make their appearance at the anode. Positive colloids like ferric oxide act exactly oppositely.

Some practical suggestions have been made for employing these facts in the separation of the radio-elements. If the added colloid is precipitated by addition of a suitable precipitant, such as aluminium sulphate, all the radioactive products are precipitated with it. It is easy in this way to concentrate a very powerful radioactivity upon a few milligrams of a precipitated hydrosol of gold or platinum. Again, positive hydrosols are precipitated in the pores of filter paper, whereas negative hydrosols pass through with the aqueous solution. According as aluminium sulphate or hydrochloric acid, on the one hand, or citric acid on the other, is added to the colloidal solution, the amount of positive or negative hydrosol, respectively, is increased, and the amount retained by filter paper may be increased or diminished. As very pure filter paper may be used and burnt after it has adsorbed the radio-element, a method of concentrating the latter is suggested. It has been found possible to separate uranium X from a uranyl nitrate solution, at a dilution of 10 gr. per litre, by simple filtration and ignition of the filter paper.

Some Obscure Problems.—The, sometimes, unexpectedly

sharp and definite chemical and physical behaviour of these almost inconceivably small amounts of the radio-elements itself raises many questions of the highest general interest. The great advances made have been largely due to the clear and consistent recognition of the important conclusion inherent in the theory of atomic disintegration, that radio-elements are completely normal and ordinary in their behaviour and in no way to be distinguished from inactive elements, during their whole period of existence. Their radioactivity is an instantaneous phenomenon terminating that existence, but not modifying or affecting them previously, though sometimes, as in recoil phenomena, giving them at the moment of production, certain nascent peculiarities of their own. This, of course, is the antithesis of the natural attitude of any one approaching the subject for the first time, who would be tempted vaguely to ascribe any abnormalities encountered in their behaviour to their possession of radioactive properties. But as our understanding of the subject becomes deeper, it may probably be necessary to make some distinction between the chemical and physical properties of radioactive and inactive elements, respectively, owing, not directly to their disintegration as such, but to the liberation of electric charges during the disintegration. Such charges may or may not, according to the conditions, neutralise one another, and in any case they are likely to be more enduring in their effects than the recoil phenomena, for example, just alluded to.

One of the earliest examples of the extremely sharp and definite behaviour of almost inconceivably small amounts of the radio-elements was furnished by the condensation of the emanations at low temperature. Since then many equally definite examples of differences in volatility of successive products in a series have come to light, and indeed this affords one of the general methods of separation employed.

Much work has been done on the condensation of the emanations, without entirely elucidating the nature of the process. The vague idea that every substance has a vapour pressure at every temperature, and that, if it were possible to follow the vapour-pressure temperature curve into the region of infinitesimal pressures, it would be found to approach a zero value asymptotically rather than abruptly,

does not accord well with the facts disclosed in the study of the condensation of the emanation. In a state of comparative purity, the radium emanation exhibits a vapour pressure curve very analogous to those of the other inert gases. When in considerable relative quantities, a small vapour pressure seems to exist even at the temperature of liquid air, for the emanation condensed at the latter temperature may be slowly and continuously pumped away by a mercury pump. But in the smallest quantity, the completeness with which it is removed from admixed air, for example, by passing through a tube cooled in liquid air, is very remarkable, and points to some effect of the absolute quantity on the vapour pressure which is foreign to our experience with ordinary liquids. Minute droplets of condensed liquid may be expected to have a higher vapour pressure than drops of a larger size, but here we have, on the one hand, the complete removal from a gas of a minute quantity of emanation at liquid air temperature, and on the other, the steady vaporisation at the same temperature of far larger quantities of the emanation from a considerable quantity of condensed emanation in vacuum. There is also some evidence of a maximum of vapour pressure, a point, that is, from which both by raising and lowering the temperature the vapour pressure is reduced. Possibly this is the explanation of the fact, first noticed by Rutherford, that, in a tube containing radium emanation immersed in liquid air and left for some time, the emanation leaves the place where it first condensed, although this is kept below the level of the liquid air and concentrates in a ring a few millimetres above the surface of the liquid air, at a place, that is, some few degrees above the minimum temperature. If the tube be then further immersed, in the course of time the ring of condensed emanation, as revealed by the fluorescence of the glass, mounts to its former position relative to the level of liquid air.⁴⁹

Making all allowances for the secondary effects of radioactivity, the heat liberated during the disintegration, the disturbance produced by recoil, and the liberation of free charges of electricity, and for effects analogous to adsorption on the walls of the containing vessel, it would appear that the phenomena encountered in the condensation of the

emanation are not fully elucidated. Further study might lead to important new light being thrown on the process of vaporisation and condensation, analogous to that already thrown on electro-chemical phenomena.

Nor, on the chemical side, is the sharpness of many chemical separations of the radio-elements entirely to be anticipated. Often, no doubt, there are causes which contribute to make the behaviour of the radioactive substance more definite than could be foreseen, and one of these is undoubtedly the presence of other substances with similar properties. Thus in a solution containing barium and radium, the radium may be precipitated quantitatively by sulphuric acid although present in quantity so minute that it is inconceivable that the radium sulphate would not be completely soluble if the barium were not present. It is, however, significant that the radium in such a system will redissolve again in the course of time if alternately heated and cooled and agitated.⁵⁰

If one took the simple theory literally, before any precipitate could be formed, the solubility product of the ions must attain a certain value. But, in the vast majority of cases dealt with, the concentration of the radio-element is far below the saturation value of the most insoluble substances known. Yet, frequently, the precipitation of the radio-element with a precipitate of a substance, chemically similar but not identical, is extraordinarily perfect. It is clear that whatever may be the conditions of final equilibrium, a very rough similarity between substances results in their replacing one another in the initial precipitate produced, though the one may be in concentration nowhere approaching its true solubility product in the radio-chemically pure state.⁵¹

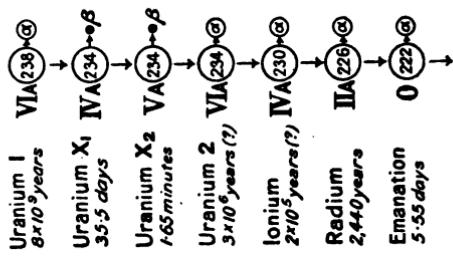
Lastly, what is perhaps even more surprising, some of these radio-elements, even in the radio-chemically pure state, especially in neutral solutions, are found to exist in the colloidal state. Here again, since the concentrations are far below the probable solubilities, it is clear that the aggregation into colloidal particles cannot be due to completely known causes. It has been suggested that what in fact may occur is the adsorption of the atoms of the radio-elements by existing colloidal particles in the solution, such as those

of aluminium hydroxide or silica, derived from the walls of the containing vessels. But, if this were so, it would mean that such existing colloids must exercise a selective action, adsorbing some and not others of the radio-elements present. The radio-elements offer exceptional facilities for the nearer study of adsorption phenomena, and it may be expected that along these lines the, at first sight, very inexplicable facts in connection with the definiteness of the physical and chemical behaviour of matter in infinitesimal quantity may find a further explanation.

SYSTEMATIC DESCRIPTION OF THE RADIO-ELEMENTS

URANIUM (U)

URANIUM I AND URANIUM 2



	Uranium 1.	Uranium 2.
Atomic weight . . .	238.15	234 (estimated to nearest unit).
Period of average life . . .	About 8,000,000,000 years.	About 3,000,000 years (?)
Radiation . . .	α -rays	α -rays
Range of α -rays (cm. of air)	2.37	2.75
Parent	Uranium X ₂ (?)
Disintegration product	Uranium X ₁	Ionium (?)

Note on Uranium 1 and Uranium 2. — Right at the commencement of the series, we are faced with the necessity of considering a chemical element, hitherto regarded as homogeneous, to be a mixture of two chemically identical or isotopic elements, the second the product of the first after one α -ray and two β -ray changes (see Part II, p. 17). The evidence of this is necessarily indirect, for the product uranium 2 is too long in period for it yet to have been grown from its supposed parent in detectable amount. The main evidence is that uranium gives two α -particles of slightly different range per atom of uranium disintegrating. The period of uranium 2 has been deduced from the range of its α -rays (p. 28) as about 3,000,000 years, and, if this is correct, it follows that there must be about one part of uranium 2 in every three thousand parts of uranium 1 in all "uranium." Its estimated atomic weight is 234 instead

of 238, so that the error in the determination of the atomic weight of uranium on this account is negligible.

The division of uranium into uranium 1 and 2 is of purely theoretical importance at present. Practically, the substance behaves as a homogeneous radio-element, giving two α -particles per atom disintegrating. By no known process has it yet been found possible to disturb the existing equilibrium ratio, and though fractional diffusion of the solution, or better of a volatile compound, would, no doubt, effect a separation, this has not yet been done. But if such a separation were possible, then one would expect to divide uranium into two parts, the one consisting of some 99.96 per cent. of the whole mass retaining only one half of the α -radiation, the other only 0.04 per cent. of the whole mass but possessing the other half of the α -radiation. Thus, if pure uranium 2 could be isolated, it would be about 1300 times as radioactive as ordinary uranium, mass for mass. The slightest alteration of the concentration of the two constituents could thus be readily detected experimentally, and the case is a very favourable one for further investigation. An experiment by the author in which uranyl nitrate was placed at the bottom of a long tube, which was then carefully filled with water, did not, after diffusion had been in progress for over a year, lead to any detectable increase in the uranium 2 in the upper layers.

Occurrence.—The most important deposits of uranium, radium, &c., occur as pitch-blende or uraninite (chiefly U_3O_8) at St. Joachimsthal, Bohemia, which, however, produces relatively less than formerly; at Johann Georgenstadt, Saxony; in Cornwall, England; in North Carolina and Connecticut, U.S.A. It has been found in small quantities but very high quality in German East Africa, and recently considerable amounts of an exceedingly rich uraninite have been found in India. Another important ore is carnotite (uranium potassium vanadate, $K_2O, 2UO_3, V_2O_5, 3H_2O$), found chiefly in the U.S.A. It comes into the market containing 2%, or more, of uranium oxide (U_3O_8), and the residue, left after extraction of the uranium and vanadium, forms the chief, if not almost the only, important source of radium in the large quantities in which it is demanded for medical uses to-day. Another ore is autunite, found first at Autun and now in

Guarda, a district of Portugal, a uranium and calcium phosphate, $\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$, occurring in pockets in very pure condition, but for the most part as a very low grade ore, bearing from $\frac{1}{2}$ to 1 per cent. of U_3O_8 . More recently, some Australian minerals have assumed technical importance. These are usually very complex and refractory. The best known is that from Olary, South Australia, where it occurs in a lode formation of magnetic titaniferous iron, magnetite and quartz, in association with biotite. As worked up at Sydney for radium, the crushed ore is first concentrated magnetically, and the 30 % of the whole, so obtained, contains 1.6 % of U_3O_8 , 0.86 % of V_2O_5 , 45.85 % of TiO_2 , 12.7 % of SiO_2 , 3.27 % of rare earth oxides, 17.4 % of Fe_2O_3 , and 16.9 % of FeO .⁵² Almost all the thorium minerals (*q.v.*) contain a certain quantity of uranium and radium. In thorianite, which contains about 60 % ThO_2 , the quantity of uranium varies usually from 10 % to 20 %, and may reach as high as 30 %.

Chemical Properties.—Like iron, uranium forms two series of salts corresponding with the oxides UO_2 and UO_3 . The common black oxide U_3O_8 , formed by heating other oxides in air or oxygen, is regarded as a compound of these, $\text{UO}_2 + 2\text{UO}_3$. The higher oxide is acidic, like chromic oxide, CrO_3 , and forms salts with alkalies, known as the uranates, having usually analogous composition to that of the dichromates, as, for example, $\text{Na}_2\text{U}_2\text{O}_7$ and $\text{K}_2\text{U}_2\text{O}_7$. Uranium is, however, less acidic than molybdenum and tungsten, the other members of the family. Salts of the lower oxide UO_2 , as, for example, UCl_4 , are not usually met with in ordinary work, as, like ferrous salts, they are powerful reducing agents, and are readily oxidised even by air. In absence of iron, uranium may be conveniently estimated by reducing it in sulphuric acid solution by zinc or magnesium, and titrating the solution with permanganate. The uranous salts are usually green.

The commonest compounds of uranium, however, are the uranyl compounds, which are usually yellow. These contain the divalent radical (UO_2), and are derived from the higher oxide UO_3 , just as sulphuryl chloride SO_2Cl_2 may be regarded as derived from SO_3 . Thus in acting on the higher oxide UO_3 with hydrochloric acid, the product is

uranyl chloride (UO_2Cl_2). Uranyl nitrate, $\text{UO}_2(\text{NO}_3)_2 + 6\text{H}_2\text{O}$, is the commonest salt, and is distinguished by its magnificent crystals, showing a yellow-green fluorescence, and by the readiness with which it crystallises from concentrated aqueous solution. This is the method by means of which uranium salts are usually purified on a large scale. The crystals melt in their water of crystallisation at about 50° , and lose their water and decompose, with evolution of nitrous fumes and formation of UO_3 , when heated gently on the sand bath. The salt, both hydrated and anhydrous, dissolves readily in common ether, and this property is frequently made use of in analysis and small scale preparations for separating uranium from minerals. On a large scale the distillation of the ether from the solutions of uranyl nitrate is apt to result in violent and even dangerously explosive oxidation of the ether unless large quantities of water are added before distillation. In this reaction an amorphous yellow insoluble compound of uranium, having the approximate composition UCH_4O_6 , is formed. It decomposes readily at 220° - 300° , with loss of CO_2 and H_2O , forming a basic uranous carbonate. It is soluble in ammonium carbonate solution, and has not been previously described.

The property of most value, however, in the separation and analysis of uranium, is the solubility of the uranyl salts of all the common weak acids, such as carbonate, phosphate, &c., in alkaline carbonates. Ammonium carbonate is usually employed, as this reagent on heating dissociates into ammonia and carbon dioxide, which completely escape from the solution, so that the uranium is reprecipitated completely by simple evaporation. But sodium and potassium carbonates are equally effective, and are sometimes preferable.

Separation and Estimation.—In the technical assay of uranium in pitch-blende, what is known as Patera's method is practised at the State mines of Joachimsthal. The pitch-blende is dissolved in nitric acid, poured into moderate excess of sodium carbonate and filtered, preferably after standing for some hours to insure complete separation of the iron. The operation may be repeated on the precipitate, if necessary, but under proper conditions the whole of the uranium is contained in the solution practically free

from other constituents of the mineral, and may be precipitated as sodium uranate by acidifying, boiling off the carbon dioxide completely, and adding sodium hydrate. The precipitate is filtered and ignited without washing, washed free from alkali, and weighed as sodium uranate.

This pouring of a solution of uranium containing a complex mixture of other constituents into excess of an alkaline carbonate is always a valuable first step in the separation of the uranium, and when the latter element is the only one being separated or estimated, it affords a ready means of obtaining the whole of the uranium in the filtrate in a state of approximate purity. For analytical estimations it is almost always an advantage to add some ammonium sulphide to complete the precipitation of the iron. Any suitable method can then be employed for the separation and estimation of the uranium in the filtrate. One of the most commonly employed is, after acidification and removal of the carbon dioxide, to add microcosmic salt (sodium ammonium hydrogen phosphate), to neutralise as nearly as possible with ammonia without causing a permanent precipitate to form, and then to add a considerable excess of sodium thiosulphate. Boiling for ten minutes brings down the whole of the uranium as phosphate with a bulky sulphur precipitate which settles and filters excellently. After washing, the precipitate is ignited at a dull red-heat and weighed as the "green phosphate," a body which has been found empirically to correspond with 68.55 % of uranium, and which is far less hygroscopic than the pyrophosphate. When pure it dissolves completely in concentrated nitric acid, but when impure the solution is more difficult. Evaporation of this solution and ignition leave the yellow pyrophosphate $(\text{UO}_2)_2\text{P}_2\text{O}_7$, which contains 66.81 % of uranium. The conversion of the "green phosphate" in the crucible into the yellow pyrophosphate affords a check on the estimation, but the latter body is excessively hygroscopic and difficult to weigh. (For further details, Brearley's *Analytical Chemistry of Uranium* should be consulted.)

Uranium may also be precipitated as ammonium uranate, and ignited and weighed as U_3O_8 . The only difficulty is the washing of the precipitate, which must be done with a 4 % ammonium nitrate solution, as water causes the

precipitate to become colloidal and run through the filter. Another method is to precipitate uranium with ammonium hydrate and sulphide, as uranous oxide UO_2 , and to weigh as such after ignition in hydrogen, or as U_3O_8 after ignition in oxygen. Autunites and similar phosphates containing calcium are best estimated as phosphate, acetic acid being present to prevent the precipitation of the calcium.

An excellent colorimetric method of estimating uraninum, applicable to very dilute solutions, is to add to the solution and to a similar volume of water in small evaporating basins the same amounts of potassium carbonate solution and half a gram or so of sodium peroxide. The intense yellow colour due to uranium is visible in extremely dilute solutions, and is more easily matched when faint. The colour in the basin containing the uranium is then matched with that of the blank by running into the latter standard uranium solution. Iron interferes badly with the tint. It is best removed by treating the uranium solution with the ammonium hydrate, carbonate, sulphide mixture as described. A tenth of a milligram of uranium can readily be detected, and, with care, estimated in this way. The method is of value in the rapid examination of precipitates, &c., obtained during the separation of uranium, to test whether all the uranium has been removed.

Treatment of Radioactive Minerals.—The radioactive constituent of uranium minerals of greatest technical value is, of course, radium, whereas the valuable constituent in the case of thorium minerals is mesothorium, which has identical chemical properties. Hence they are always separated together, if present, and the same treatment is applicable to both. The older methods were largely developed in consequence of the existing practice in the treatment of uranium minerals. These were fused with sodium sulphate, and the uranium lixiviated out with water and dilute sulphuric acid, the insoluble residues containing the radium and radio-lead as sulphate, and part of the ionium, polonium, and actinium. Probably these residues are now no longer obtainable. The separation of the radioactive constituents has become at least as important as the separation of the uranium, and starting with fresh mineral *ab initio*, far simpler methods could be devised according to the character of the

mineral. Many of the minerals, for example, carnotite, autunite, and thorianite, are soluble in dilute acids, and from such solutions, by pouring into sodium carbonate, the uranium can be at once recovered from the filtrate, whilst the radium and other active constituents are precipitated as carbonates in a form very easily redissolved and further concentrated. No doubt, gypsum, if present, would prevent the radium going into solution, and in such cases the older methods might have to be resorted to. In the case of pitch-blende, which is soluble in nitric acid, the existence of sulphides causes sulphates to be produced, and part of the radioactive materials is precipitated as sulphates. But such precipitation can often be prevented by use of concentrated acid until the solution has been separated from the bulk of the insoluble material, and the amount of material to be worked up for radium could no doubt be enormously reduced if desired. But sooner or later the separation of the radium and mesothorium, if present, which constitute the two most important of the radioactive constituents, is effected through the insoluble sulphates and their separation with barium sulphate. This method will be referred to under *Radium*, but for full details of the factory processes the originals must be consulted.⁵³ When the active elements have been precipitated with the insoluble sulphates a considerable concentration, in the laboratory, can often be effected before solution of the active material by treatment with 25% sodium acetate solution, which dissolves the lead sulphate and part of the calcium sulphate.

In the working up of the Olary ore, in which the first treatment of the magnetically concentrated material is a fusion with salt cake (acid sodium sulphate), it was found that it is only necessary to decompose about half the ore to secure a practically complete yield of the radioactive contents, and on this fact the successful economical treatment of such low-grade material largely depends. The undecomposed mineral, which is free from radioactive constituents, settles out more quickly from the aqueous liquors than the part decomposed, and may be at once rejected by this means.⁵²

Radioactivity.—All uranium salts, and uranium itself, in ordinary circumstances give, in addition to the α -radiation,

an important and fairly penetrating β -radiation, due to uranium X. The latter is easily separated in most of the processes of purification in vogue, so that freshly prepared uranium salts gave at first only α -rays. The β -rays are gradually regenerated. After about three weeks from purification they are nearly half the ordinary equilibrium strength, equilibrium being practically reached after from six months to a year.

Standards of α -Ray Activity.—On account of the constancy of the α -radiation of uranium, which, till now, has not been diminished or affected by any chemical process, the most convenient standards of radioactivity to employ in the standardisation and calibration of electroscopes and other measuring instruments employed in radioactive work, are made of thin films of black oxide of uranium U_3O_8 . The commercially pure uranyl nitrate may be further purified by one of the methods previously alluded to, either by crystallisation, solution in ether, or pouring into ammonium carbonate. It is then cautiously ignited in a platinum crucible. The ignition is continued on the blast in a current of oxygen, which is maintained after the heating is stopped. The pure black oxide is ground up in an agate mortar with freshly distilled chloroform to a thick paste. By means of a clean camel-hair brush, shallow circular copper trays of definite area are coated with the smallest quantity of the paste necessary completely to cover the surface, and the chloroform is then allowed to evaporate spontaneously.⁶⁴ An alternative and, in the author's hands, preferable method is to grind up with water, instead of chloroform, and spread on a ground glass plate by means of another small ground plate cemented to a cork as handle. The films are then dried in the water oven.

The α -radiation from the trays is proportional to their area, and, so long as the surface is completely covered, is quite independent of the amount of material used to cover them. Provided no more of the uranium oxide is used than is necessary to cover the surface, the β -radiation is practically negligible. For very accurate work it is advisable to use a preparation of uranium oxide, which has been prepared for some months, of which the β -radiation is constant. Such standards are, of course, used bare, but are

kept covered to protect them from dust when not in use. They are easily prepared, and the film adheres well to the surface. By preparing similar films of minerals or other materials and comparing their discharging action on an electroscope with that produced by the standard uranium film, the α -activity of the substance in terms of that of U_3O_8 may at once be accurately determined by means of a simple electroscope. The total α -activity of a uranium mineral is 4.64 times that of the uranium it contains if there is no thorium present. Hence by dividing the activity of the mineral in terms of that of U_3O_8 by this factor, a rough evaluation of the proportion of the contained U_3O_8 may be made. If larger quantities are available, a γ -ray test is always preferable. (See *Radium*.)

Uranium and uranium X form for practical purposes a distinct and complete disintegration series in themselves, which is connected with the long ionium-, radium-, radio-lead-, polonium series on the one hand and the actinium series on the other only by indirect theoretical reasoning. For in spite of the most exhaustive and delicate experiments, no direct production of ionium, radium, or actinium has so far been observed from uranium. Neither from the uranium X, separated from 50 kilograms of pure uranyl nitrate, was there observed any production of a radioactive product,⁵⁵ though, theoretically, uranium 2 should be formed from uranium X. For all practical purposes the decay of the activity of uranium X is as complete as that of polonium, the end member of the radium series, or of thorium C, the last member of the active deposit and of the series of thorium. With this may be contrasted the decay of radium C, the last member of the active deposit of radium, the decay of which is only apparently complete. Really the activity falls to a very small value, and then steadily increases again for many years, due to the formation of later products which are radioactive. The extreme simplicity of the uranium series proper, which contains only two radiating substances, one giving all the α -rays and the other all the β -rays, the comparatively short period of the β -ray producing product, and the absence of all slowly changing or gaseous products of disintegration, make the compounds of uranium especially adapted for use as standards of radioactivity and for illus-

trating the main principles of radioactive change in their least complex aspect. In fact uranium expels two α -particles per atom disintegrating, and is not a single element, but a mixture of two, chemically non-separable, differing in atomic weight by four units, and both expelling α -rays. Such a mixture, however, acts as a single element expelling two α -rays per atom, and this theoretical complication in no way interferes with the practical simplicity of the case referred to.

URANIUM X₁ AND URANIUM X₂.

	Uranium X ₁ .	Uranium X ₂ .
<i>Estimated atomic weight</i>	234	234
<i>Period of average life</i>	35.5 days.	1.65 minutes.
<i>Radiation</i>	β -rays.	β - and γ -rays.
<i>Absorption coefficients</i>	$\mu_{(\beta)}\text{Al} = 510$	$\mu_{\beta}\text{Al} = 14.4$ $\mu_{(\gamma)}\text{Al} = 24$ $\mu_{(\gamma)}\text{Al} = 0.70$ $\mu_{\gamma}\text{Al} = 0.14$ $\mu_{\gamma}\text{Pb} = 0.72$
<i>Chemical analogue</i>	Isotope of thorium.	Homologue of tantalum.
<i>Parent</i>	Uranium 1.	Uranium X ₁ .
<i>Disintegration product</i>	Uranium X ₂ .	Uranium 2.

Like uranium, its product, uranium X, has recently been analysed into two distinct radio-elements, the difference being that, in this case, the products are successive and both give β - instead of α -rays. The exact position, only, of these two products in the series is a matter of theory rather than experiment. For any experimental evidence to the contrary, they might be regarded as the products of uranium 2 rather than of uranium 1. But the α - and β -ray change rules, to be obeyed, necessitate that the series should run as shown on p. 70, and hence this is generally accepted (see Part II, p. 17). Uranium X₂, also named brevium, being a very short-lived product, is always present in equilibrium amount with uranium X₁, except during the first few minutes after separation. It is convenient to consider first the two products together as one, under the old name "uranium X." The chemical reactions refer, naturally, to those of the

longer-lived uranium X, the radioactivity to a mixture of the two in equilibrium.

Uranium X is responsible for the penetrating rays of ordinary pure uranium compounds, and may be easily separated by many of the methods of purification described under *uranium*, only, of course, to be re-formed with the lapse of time. Thus, on crystallising uranyl nitrate by allowing a hot solution, of sp. gr. 2.05, to cool, about two-thirds of the salt crystallises, and the mother liquor contains about six-sevenths of the uranium X present. On shaking crystals of the same salt with ether, two layers are formed, of which the lower aqueous layer retains the whole of the uranium X.⁵⁶ Other solvents, such as acetone, various alcohols, ethyl and methyl acetate, have been recommended, but it is doubtful if they offer any advantage. In all such cases the solution in the organic solvent may be shaken with freshly precipitated ferric hydroxide and filtered, which makes the separation easier in unpractised hands. On pouring a uranium solution into excess of a solution of carbonate of sodium or ammonium, the iron, alumina, and other impurities are precipitated, and these retain the whole of the uranium X. If the uranium is too pure, it is necessary to add a little ferric salt to serve as a nucleus for the uranium X. It may be separated from iron by dissolving the precipitate in concentrated hydrochloric acid and extracting the solution with ether saturated with hydrogen chloride, when the uranium X remains in the aqueous layer.⁵⁷ In the ammonium carbonate process the uranium X precipitate, if too great, may be redissolved in acid, and poured into very concentrated ammonium carbonate, and the solution reprecipitated fractionally by boiling. According to the nature of the other substances present, the uranium X comes down sharply and definitely with one of the fractions, usually in the middle of the series.⁵⁸

Uranium is readily absorbed by the action of barium sulphate formed in the solution or by carbon. Soot, obtained freshly by burning naphthalene, has been recommended. It is always difficult or impossible to remove uranium X completely by these means. Perhaps owing to the common presence of thorium as an impurity, they are apt to be rather uncertain. The addition of thorium

to the uranium solution and its precipitation in acid solution with hydrofluoric acid has been recommended as a method of separation of uranium X from uranium.⁵⁸

If the uranium X is required as free as possible from all other substances, a carefully purified rare earth, such as lanthanum, may be added instead of thorium. After separation, the solution of the rare earth is precipitated with sodium thiosulphate. Sufficient thorium is usually present to insure that the uranium X is precipitated with the sulphur formed, so that after ignition only a very minute residue is left. Uranium X has not been volatilised by heating in air.

The foregoing separations refer, of course, equally to the separation of uranium from thorium, reading throughout thorium for uranium X, so long as the thorium is present in minute quantity. But a mixture of uranium and thorium in similar proportions behaves entirely differently. With less than 10 % of thorium nitrate present with uranyl nitrate, no thorium could be detected in the ethereal extract of the aqueous solution. But with a mixture of 50 % of each nitrate, large quantities of thorium as well as uranium dissolve in the ether. So also in the ammonium carbonate separation, the thorium, if present in any quantity, redissolves in excess of the ammonium carbonate, but is reprecipitated by boiling, long before the uranium.⁵⁴

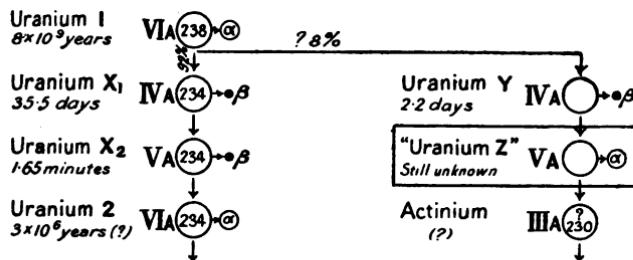
The radiation of "uranium X" is characterised by a β -radiation, which is only slightly less penetrating than that of radium C, the most penetrating known. When passed through absorbing screens, the absorption proceeds very nearly exponentially until by far the greatest part is absorbed. Using very active preparations and studying the process of absorption over several millimetres of aluminium, until the radiation is reduced to a few ten-thousandths of its initial value, a regular increase in the absorption coefficient to two or three times its initial value is observed.⁵⁹

In addition to this radiation there is a very soft (β)-radiation, which was at one time mistaken for an α -radiation. Working with a bare film, under ordinary conditions, it produces an ionisation somewhat greater than that produced by the β -rays, but it is inappreciable through 0.1 mm. of aluminium.

The γ -radiation is extraordinarily feeble, relatively to the β -radiation, in comparison with radium C, mesothorium 2 or thorium D, the other γ -ray producing radio-elements. It is also somewhat less penetrating.⁶⁰ Recent work has disclosed in addition (γ)-rays of two types, one less penetrating than the β -rays and the other intermediate in penetrating power between the β - and γ -rays.⁶¹

Analysis of "Uranium X" into Uranium X₁ and Uranium X₂.—Uranium X₁ is the isotope of thorium, and uranium X₂ is analogous in properties to tantalum. If uranium X is subjected to any operations, capable of separating these two elements with sufficient speed, it will be found that the β -rays come from the portions resembling tantalum, and, after separation, these rays decay completely with a half-period of about 1.5 minutes. Thus, filtration of the uranium X solution through a filter containing a few milligrams of moist tantalic acid effects a partial separation. The portion resembling thorium at first gives only (β)-rays, and proceeds to regenerate the β -rays at the corresponding rate, the half value being reached 1.5 minutes after separation and the equilibrium value after some 15 minutes. It is not yet known how the γ -rays originate, but it is usually assumed that they accompany the β -rays in the disintegration of uranium X₂. With regard to the (γ)-rays nothing is yet known or can be inferred.

URANIUM Y



Estimated atomic weight—234 or 230.

Radiation—(β)-rays.

Absorption coefficient— $\mu_{(\beta)}\text{Al}$ = about 300.

Chemical analogue—Isotope of thorium.

Parent—Either uranium 1 or uranium 2.

Disintegration product—Unknown.

There is an abnormality in the decay of the (β)-rays of uranium X₁, whereas the β -rays decay perfectly normally. It affects only about 10 % of the total (β)-radiation, and this portion is distinctly more penetrating (μ_{β} , Al = about 300) than the rest. But if the uranium X₁, after having been completely separated from the uranium, is allowed to reform for a few hours only before re-separating, then it will be found that the abnormal part of the (β)-radiation is relatively very much increased, and may be many times greater than the normal part. Under such conditions it is very much easier to study.

Instead of this part decaying like the β -rays with the 24.6 days half-period, it decays much more rapidly, to half value in about a day, and therefore must be due to a new product, termed uranium Y.⁶² The elucidation of the problem presented considerable difficulty, partly on account of the minuteness of the effects and also for another reason. It has been shown that uranium Y and uranium X₁ are isotopic and therefore non-separable, and that they are *simultaneously* produced from uranium. The much quicker period of the former results in the proportion between the two isotopes being the greater the shorter the time of accumulation, and so, as detailed above, the effect of the former may be increased relatively to that of the latter. The lapse of time may be used to produce a change of concentration between the two isotopes, which chemical methods are quite unable to effect. The scheme shown above is the most probable.

It is supposed that either uranium 1 or uranium 2 (the first is depicted in the diagram) undergoes a dual change, in both of which α -rays are expelled. In the first mode, which claims some 92 % of the atoms disintegrating, uranium X₁, and in the second mode, which claims the remaining 8 %, uranium Y is the product. Both, being formed from uranium in an α -ray change, are isotopic with thorium. Both give (β)-rays, those of uranium Y being somewhat the more penetrating, in accordance with its shorter period. But the product of uranium Y remains experimentally unknown. It is called "uranium Z" in the diagram. It must be an isotope of uranium X₂, in the "eka-tantalum" place in the Periodic Table, and it must be long-lived to have

escaped detection. *If* it gave α -rays on disintegration it would produce a member isotopic with actinium, or actinium itself. It is extremely probable that it does this, and that the actinium series is joined to the uranium series, through uranium Y and such an unknown long-lived eka-tantalum, giving α -rays, but this remains to be proved. Even if this is done it would still remain doubtful whether uranium 1 or uranium 2 is the starting point of the series, as either would fit the case equally well. It is perhaps a little unfortunate that the cases, without exception the most difficult to elucidate experimentally, should come at the very commencement of the uranium series, and therefore fall to be dealt with first. For there is nothing in the whole of the rest of the series so complicated or difficult to put to experimental test as are the precise relations between uranium 1, uranium 2, uranium X, uranium Y, ionium and actinium. Nevertheless the scheme outlined is extremely probable. It is only the difficulties due to the enormous life-period of some of the members which prevent it from having been as yet completely put to the proof. If any one took the trouble to put the precise signification of the above diagram into words, it would rather be a matter for surprise, not that we still have to build to some extent on conjecture, but rather that in the short period since radioactivity was discovered it has been found possible to learn so much.

IONIUM (Io)

Estimated atomic weight—230.

Period of average life—Probably between 100,000 and 200,000 years.

Radiation— α -rays.

Range of α -rays—2.85 cm. of air.

Chemical analogue—Isotope of thorium.

Parent—Uranium 2 (?).

Disintegration product—Radium.

The existence of this substance, an intermediate product of long-life between uranium X and radium, was foreshadowed by the minuteness of the growth of radium in uranium preparations purified from radium. It was discovered and isolated from pitch-blende and other uranium

minerals by Boltwood.³⁶ In the preliminary treatment of the mineral it is separated with the actinium, and indeed the first actinium preparations separated owed their radioactivity almost certainly in part to admixture with ionium. It is, however, easily separated from actinium.³⁷ Its chemistry can be fully and accurately described in a single sentence. It resembles thorium in its whole chemical nature, as far as it is known, with absolute completeness, so that not only is no separation of the two elements possible by any known method, but no concentration of the one constituent with reference to the other has been accomplished. Such an alteration of concentration could be readily detected, if it occurred, even with the infinitesimal amounts of ionium used, because of the intense α -activity of the latter. It must be remembered that the chemistry of thorium has been closely and exhaustively studied on account of its resemblance to and association with many other rare earths of no technical value, and in consequence a large number of characteristic and effective methods for the purification of thorium from all other elements are known (see *Thorium*).

A certain and easy method of separating ionium from any mixture is to add thorium thereto, if not already present, and then to separate the thorium and subject it to a rigorous purification process by the ordinary methods. This is a general method adopted in radioactivity. It is doubtful if ionium free from thorium has been prepared. Cerium, carefully freed from thorium, has been employed for the separation of ionium, for example, by precipitation with hydrofluoric acid in strongly acid solution. The cerium may then be separated from ionium by the methods used to separate it from thorium. However, there is probably some thorium in all uranium minerals. In Joachimsthal pitch-blende the quantity is extremely small, but, in the working up of thirty tons of mineral, Auer von Welsbach accumulated a few grams of pure thorium containing the ionium of the mineral.³⁷ The nitric acid solution of pitch-blende, after removal of lead, &c., by sulphuric acid, may be precipitated directly with hydrofluoric acid. The fluorides are dissolved by boiling with sulphuric acid and fractionally precipitated by zinc hydroxide paste. The first precipitate contains all the thorium and ionium present.³⁸

In the working up of thorium minerals, the whole of the ionium associated with the uranium present remains with the thorium. As practically all thorium minerals contain some uranium, all sources of thorium contain some ionium, the preparations obtained from monazite containing less than those from thorianite, and those from Ceylon thorite least of all. It must be remembered that the period of thorium is about 3.6 times that of uranium. In consequence, the α -activity of thorium, free from its own products, separated from a mineral like Ceylon thorianite, containing, for example, 60 % of thorium and 16 % of uranium, would consist of the α -rays of ionium and of thorium in similar amount. In all commercial thorium the α -radiation of the ionium present is a considerable fraction of that due to the thorium itself. If we reckon monazite to contain 0.3 % of uranium and 4 % of thorium, about one-fifth of the α -radiation ascribed to thorium itself, in commercial thorium preparations, would be due to ionium.

The most characteristic feature of the radioactivity of ionium is its power of producing radium steadily with the lapse of time. The radium may be easily separated from the ionium, for example, by precipitating barium sulphate in the solution, but in course of time it continuously reforms. It is usually detected by means of the characteristic radium emanation, the solutions being kept in sealed flasks and the gases accumulating boiled out from time to time and introduced into an air-tight electroscope. Owing to the long period of ionium the amounts of radium so formed are, of course, extremely minute. As a consequence of what has already been said, it follows that all thorium preparations generate radium, to a greater or less extent, according to the amount of uranium in the minerals from which they were derived. Otherwise, ionium, in the radioactive sense, is very similar to polonium, its radioactivity consisting of low-range α -rays only. It possesses the great advantage over polonium for many purposes, in that its radioactivity is constant and does not sensibly decay. It will no doubt find large application where a steady, powerful source of α -radiation is required, as in compensation methods of radioactive measurement and for α -ray standards more active than those of uranium. The proportion changing into

radium, even in a lifetime, is so small that it may in most cases be neglected. It is only by refined emanation tests that it can be detected.

The period of ionium remains uncertain. The period cannot be greater than a million years, because of the intense α -activity of the ionium preparation separated by Welsbach. Even if these were pure ionium, free from thorium, the period, as estimated from the activity, would not exceed the maximum stated. To get the real period this maximum must be reduced by the factor representing the unknown proportion of ionium present with the thorium in the preparation. The period estimated approximately from the range of the α -particles is 200,000 years. The author's results, on the rate of production of radium from very carefully purified uranium preparations, led, after more than ten years' work, to the *minimum* estimate of 100,000 years.⁶⁴ The most recent results with these preparations indicate that this is probably not far from the actual period, but a few more years must elapse before this can be considered definitely established.

RADIUM (RA)

Atomic weight—225.95.

Period of average life—2440 years.

Radiation— α -, (β) - and (γ) -rays.

Range of α -rays—3.13 cms. of air.

Absorption coefficients— $\mu_{(\beta)}$ Al about 200.

$\mu_{(\gamma)}$ Al = 354; 16; 0.27.

Chemical analogue—Homologue of barium.

Parent—Ionium.

Disintegration product—Radium emanation (Niton).

Occurrence.—All ores containing uranium contain radium. In the great majority of cases the ratios of the quantity of radium to that of uranium is a constant, viz. 3.23×10^{-7} , which is known as the "equilibrium ratio."⁶⁵ That is to say, 323 milligrams of radium (element) are present per ton of uranium (element). Certain minerals are exceptional in that the constant of radium is less than this. The most important of these are the autunites, for which the ratio varies from 20 % to 80 % of the equilibrium. Conversely, the only

certain case of a mineral containing radium and no uranium is a certain deposit of pyromorphite (Issy l'Evêque, France) found in the neighbourhood of autunite deposits, which are superficially coated with a radiferous layer, doubtless derived from the autunite by the action of percolating water. According to recent researches, it seems that geologically old formations contain a somewhat greater radium ratio than recent ones, but the difference, if any, is small and uncertain.⁶⁶

All common rocks and minerals of the earth's crust contain minute amounts of radium, of the order of a few million millionths of the total mass. It is found in natural springs, both hot and cold, many of the spas most celebrated medicinally containing the greatest quantities either of radium or of its emanation. There are few materials in which radium cannot be detected by the emanation test, if sufficiently large quantities are examined, but whether this has any special significance or is merely due to the almost incredible delicacy of the emanation test is not easy to decide. There is no reason to doubt that in all these common materials the three-millionfold greater equilibrium quantity of uranium is also present, although this cannot be detected chemically, owing to its minuteness.

Properties.—Radium is the most important of the new radioactive elements. It was discovered by M. and Mme. Curie in the years immediately following Becquerel's first observation of the property of radioactivity of uranium compounds in 1896. Mme. Curie formulated the fundamental principle that radioactivity is an atomic property, and this led her to the examination by chemical analysis of the uranium minerals, the radioactivity of which is several times greater than can be accounted for by the radioactivity of the uranium present. She found the radioactivity was concentrated in the second group with bismuth (polonium) and in the alkaline-earth group with barium (radium). Radium resembles barium in all the usual analytical reactions, the sulphate being even less soluble in water than barium sulphate. It is therefore the least soluble sulphate known. Radium is distinguished from barium by the lesser solubility of its chloride and bromide in water or in hydrochloric and hydrobromic acid, and this is the principle of the method adopted in its separation from barium. The physical and

chemical properties (heat of solution and of formation, solubility, facility of forming peroxides, stability of the carbonates, &c.) of the various compounds of the alkali and alkaline-earth metals usually show a well-marked graduation in the order Ca, Li, Sr, Ba, Na, K, Rb, Cs, and in this scheme radium comes between barium and sodium.⁶⁷ This may prove a valuable analogy in indicating the probable properties of the various radium compounds, which are still for the most part unelucidated.

Spectrum.—Radium compounds colour the bunsen flame a fine carmine tint. The flame and spark spectra exhibit the closest analogy to those of the other alkaline earths. The strongest line in the photographic region of the spark spectra is in the ultra violet ($\lambda = 381.47\mu\mu$). This line is visible in the spectrum of a barium salt containing only 0.01 per cent. of radium. The relative intensity of the two neighbouring violet lines, of radium 455.33, and of the strongest barium line 455.42, furnishes a good test of the completeness of separation of the elements. Even in the purest fractions of Mme. Curie the barium line was still just visible, while when 0.6 % of barium was added the intensity of the two lines became similar.

Separation and Fractionation of Radium.—The most important operations in the working up of radium-containing materials are the solution of the material, consisting usually of insoluble sulphates, and the separation of the halogen salts of the alkaline-earth group in a pure state, followed by their fractional crystallisation. The first operation is usually effected by vigorous boiling with sodium carbonate solution, filtering and washing free from sulphate. This is the well-known reaction studied dynamically by Guldberg and Waage, whereby an equilibrium is attained between the two pairs of soluble and insoluble sulphates and carbonates. Naturally the greater the excess of sodium carbonate the larger the proportion of insoluble sulphate converted into insoluble carbonate. In this operation it is advisable not to wash at once with water but with sodium carbonate solution until most of the sulphates are removed, as thereby the reconversion of the carbonates back into insoluble sulphates is largely prevented. In dealing with crude materials, for example, the radium-containing residues from pitch-blende, it

is often advantageous to precede this operation by a similar one, using a sodium hydrate solution containing a little carbonate which dissolves part of the lead and silica present. The carbonates, washed free from sulphates, are treated with pure hydrochloric acid which dissolves the alkaline earths including radium. From the solution the latter may be precipitated as sulphates by sulphuric acid and reconverted back into carbonates as before, or sometimes more conveniently they may be precipitated directly as chlorides by saturating the solution with hydrogen chloride. This is a very elegant method of great utility in the laboratory, for the most probable impurities, chlorides of lead, iron, calcium, &c., remain in solution and only the barium and radium chloride are precipitated, practically in the pure state, ready for fractionation. It has been applied successfully in the treatment of the Olary ores.⁵²

All these tedious and lengthy wet reactions could with advantage be replaced in many cases by simple reduction of the insoluble sulphates to sulphides in a current of coal gas, water gas, or other reducing atmosphere, followed by solution of the product in acids. The technical application of this method appears to present difficulties which have not yet been surmounted. Another suggested method is to mix the raw sulphates in the dry state with calcium hydride, both finely divided, and to set fire to the mixture, whereby the sulphates are reduced to sulphides.⁵³

The fractionation offers no difficulty, at least in the initial stages when the quantities of materials are large. The chloride is dissolved in boiling water in one vessel, A, to a just saturated solution and left to cool, the mother liquor is drained off into another vessel, B, again concentrated to saturation, while the crystals are dissolved to saturation in fresh boiling water. On cooling, the mother liquor of B is drained into a new vessel, C, while that of A is drained into B, and used to dissolve the crystals. The operation is repeated till perhaps five vessels are obtained. After this the number of fractions is kept constant while, alternately, crystals are withdrawn from the process at the less soluble end and the mother liquor from the other end. The crystals contain practically all the radium, and the mother liquor only a small quantity. When the crystals become very small in

quantity, through repeated fractionation, gradually increasing quantities of hydrochloric acid are added to the water used to dissolve them, so increasing the volume of the solutions handled and enabling the crystallisation of only a few milligrams of the salt to be conveniently carried out. The fractionation of the bromides is described as more rapid but less regular. The chloride is a much more stable compound than the bromide, and parts with its halogen much less readily on keeping.

Atomic Weights.—Since Mme. Curie's determination, wonderfully accurate as it now proves to have been, a very careful revision of atomic weight has been undertaken by Hönigschmid.⁶⁹ The method employed was the same as that used by Mme. Curie, the ratios $\text{RaCl}_2/\text{AgCl}$ and RaCl_2/Ag being found, the differences being mainly in minor points. The mean value obtained, 225.95, is so near the whole number, that for all practical purposes the atomic weight may be taken as 226. The individual determinations did not differ from the mean by more than 0.03. A similar set of determinations with the bromide give 225.96. By spectroscopic comparisons it was shown that the final bromide preparation employed must have contained less than 0.002 % of barium. About 1.35 grams of the purified chloride was employed.

In this connection, a revision of the atomic weight of uranium by the same investigator is of interest, in that it showed a figure, 238.15, much nearer the whole number than that previously accepted, 238.5. It is, however, still far enough from it and from that calculated from the atomic weight of radium by the addition of three times the atomic weight of helium, to raise the question whether mass is accurately conserved in radioactive changes. There is, at least, reason to believe that in these changes small losses of mass may occur, and that, among the atomic weights generally, the small and irregular departures from whole members observed may be connected with differences of energy content. A heavy atom, for example, disintegrating with evolution of energy into two lighter atoms, may suffer in the process an apparent loss of a small part of its mass. There have been a large number of new speculative attempts to find regularities among the atomic weights on the idea

that the heavier elements are compounded out of the simpler ones, and the uncertainty whether mass is strictly conserved makes such efforts and the approximate accuracy attained more legitimate now than formerly.

The International Radium Standard.—The use of the γ -ray method of comparing quantities of radium demands an absolute standard for comparison. A specially purified specimen of radium chloride, containing nearly 22 mg. of radium chloride, prepared by Mme. Curie, was compared by γ -ray methods with several preparations used in Hönig-schmid's revision of the atomic weights, and, on practically perfect agreement being found, the 22 mg. preparation was accepted as the International standard, and is now preserved at the Bureau International des poids et mesures, Sèvres, near Paris. Copies of this standard have been supplied to the National Physical Laboratory, Teddington, and to the official testing institutions of other countries, who undertake the determination of the quantity of radium contained in preparations submitted to them. The former uncertainty as to the purity of radium compounds has in this way been entirely removed.

Estimation—(1) *Chemical Methods.*—The estimation of the radium in a preparation is accomplished by a variety of methods according to the circumstances. For mixtures of pure radium and barium salts, containing an important proportion of radium in the absence of other elements, complementary to the spectroscopic test described above, is the determination of the chemical equivalent. Mme. Curie precipitated the solution of the chloride with silver nitrate, weighing the silver chloride and recovering the radium from the solution in the soluble form. The chloride of radium must be dried at 150° and weighed quickly, as it is hygroscopic. Sir William Ramsay converts the chloride into bromide by ignition in bromine vapour. The only objection to estimating the radium as sulphate, as in the case of barium, is the labour of recovering the radium in soluble form.

The solution of radium sulphate may conveniently be effected by repeated gentle ignition in a current of hydrogen or coal-gas, followed by solution of the sulphide produced in hydrochloric acid; or by boiling with sodium carbonate

solution as already described. If x is the equivalent of the mixture of barium and radium found by any of these methods, and A and $(100 - A)$ are the percentages of radium and barium respectively, obviously

$$x = \frac{A}{100} \cdot \frac{226}{2} + \frac{100 - A}{100} \cdot \frac{137.4}{2}$$

so that from the value of x , A can readily be deduced.

(2) γ -Ray Method.—The simplest and most direct way of estimating the quantity of radium in any preparation is by comparison of the γ -rays.

Provided that a standard preparation of known radium content is available, the percentage of radium in any preparation may, in the absence of mesothorium, readily be estimated by a simple comparison of its γ -radiation with that of the standard preparation. The γ -radiation is so penetrating that the absorption of the rays even in a centimetre thickness of the material is not serious, and hence this method enables substances of very different weights and densities to be roughly compared together, although it is advisable to use as a standard a substance as much as possible like the material being tested in these respects.

A better plan is to correct for the absorption in the following way. A known weight of the low-grade radium preparation is sealed into a spherical flask of known volume, so as just to fill it. Under these conditions the absorption of the γ -rays in the substance itself can be corrected for. If μ is the absorption coefficient, R the radius of the flask, and $2\mu R$ is called A , then where I is the intensity of radiation observed from the flask, and I_o what it would be if no absorption occurred, it can be shown that

$$\frac{I}{I_o} = \frac{3}{A} \left\{ \frac{1}{2} - \frac{1}{A^2} + \left(\frac{1}{A} + \frac{1}{A^2} \right) e^{-A} \right\}$$

This, itself useless, expression expands to the highly convenient and very rapidly converging series ⁷⁰

$$\frac{I}{I_o} = 1 - \frac{3}{4} \mu R + \frac{4}{10} (\mu R)^2 - \frac{1}{8} (\mu R)^3 + \frac{2}{5} (\mu R)^4 - \frac{1}{60} (\mu R)^5 \dots \dots$$

The value for μ/d , where d is the density, may be taken as 0.040; the density of the substance is taken as the weight

divided by the volume (V) of the flask, the radius R being given by $V = 4/3(\pi R^3)$. Hence μR of the above expression can be very easily found, and in most cases the first three or four terms of the expression are sufficient. In this way it is possible to compare accurately, by γ -ray methods, substances containing less than one-hundred-thousandth part by weight of radium, directly against a pure radium preparation, known in terms of the International Standard. In a large number of tests in the author's laboratory, the results of which were checked by direct emanation tests, the method was found accurate and more reliable than the emanation method.

As the γ -rays, and the same is equally true of the β -rays, do not come directly from radium, but from its products, escape of emanation must be avoided, and the preparation must have been prepared at least a month. The only perfectly rigorous method is to seal up the preparations in glass vessels a month prior to testing. But for the rapid approximate estimation of the radium in minerals this precaution can usually be omitted. This method lends itself especially to this kind of test, and is the one invariably employed by the author. A large lead* electroscope, say 20 cm. high by 20 cm. diameter, of wall-thickness 0.4 cm., the windows and exposed parts screened by lead to prevent the entrance of secondary radiation, is employed. The leaf system is the simple single leaf system insulated by a sulphur bead. In comparing pitch-blendes and other minerals, a lump of 20 to 100 grams according to the richness is simply laid on the top, and the increase of leak compared with that produced by a similar lump of a standard pitch-blende, the uranium content of which is known. Thus, as an example:

	% U.	Weight.	Leak.
Standard	60	25 g.	15 div. per min.
Specimen tested	x	40 g.	10.4 div. per min.

$$x = \frac{25}{40} \times \frac{10.4}{15} \times 60 = 26 \% \text{ U},$$

* Old sheet-lead from the roof of an ancient building is best, as the radio-lead, always present in freshly prepared lead, will have decayed, and the natural leak of the instrument will therefore be less.

and the amount of radium is $0.26 \times 0.32 = 0.083$ gram per ton of mineral.

For materials containing only of the order of one per cent. of uranium, larger quantities are necessary, and it is convenient to place them in curved shallow boxes of tinplate around the sides of the electroscope. For the standard of comparison the boxes may be refilled with a mixture of the material being tested with a known small proportion of powdered standard pitch-blende. This avoids all uncertainty due to the absorption in the material itself.

The comparison of concentrated radium preparations in sealed tubes can be done readily by the same instruments, the distance of the preparation from the instrument being varied to suit the strength of the preparation. Provided a proper lead electroscope is used, no difficulty is to be anticipated from the strong secondary radiation generated by the γ -rays in all surrounding objects, but otherwise it is important that nothing should be moved on the bench during the measurements except the active preparations themselves, and that the observer should sit motionless in the same orientation throughout the actual observations.

In the presence of thorium, the test gives still a reliable measure of the technical value of the mineral. The separable mesothorium contributes per unit about one-fifth to one-sixth of the γ -ray effect contributed per unit by the uranium, whilst the non-separable radiothorium probably contributes a like amount. The radium separated from thorium-containing uranium minerals contains also the whole of the mesothorium present. The possibility also of the wilful adulteration of radium preparations by means of the less permanent mesothorium must not be forgotten. The γ -ray test gives really in such cases the measure of the penetrating radioactivity separable as radium rather than a measure of the true radium. Thus if a mineral, containing equal percentages of uranium and thorium, appeared by this test to contain 30 milligrams of radium to the ton, the real radium content would be between 25 and 20 milligrams. After the lapse of many years, when the decay of the mesothorium has occurred, the activity would of course sink to the true radium value. In such cases one may take the γ -activity three hours after the preparation has been dis-

solved in water and evaporated to dryness again. This allows the radium emanation to escape, and after three hours the γ -activity is that due to the mesothorium alone, but it is better to use the following method in all such cases. (See also *Mesothorium*.)

(3) *The Emanation Method.*—A method applicable to solutions containing from 10^{-8} to 10^{-10} gram of radium is to seal up the solution, which must be limpid, and acid, to prevent the precipitation of the radium, in a small distilling flask, and to allow the emanation to accumulate. After one month the equilibrium amount is present, and the quantity then does not alter however long the flask is kept sealed. The emanation is boiled out of the solution into a previously exhausted gasholder, and the contents of the gasholder are admitted through a calcium chloride tube into an exhausted air-tight electroscope. The leak after three hours from admission is taken, the gold leaf being positively charged. As standards may be employed similar flasks containing small known weights of pitch-blende of known uranium content dissolved in nitric acid. If for any reason it is inconvenient to wait a month after sealing before testing, the proportion of the equilibrium amount of emanation accumulating may be taken as $1 - e^{-\lambda t}$, where λ has the value 0.0075 (hour) $^{-1}$, and t is the time in hours.⁷¹ (Tables of this function are to be found in *Le Radium*, 1909, 195.)

The carrying out of the emanation method requires great care and circumspection, if reliable results are to be obtained, owing to the tendency of the radium, either in the standards or in the solutions being tested, to precipitate out in an insoluble form in which its emanation is retained. Sulphates, obviously, must rigorously be excluded from the water and reagents employed. Old standards cannot be relied upon for the same reason, and it is necessary to calibrate the instrument used frequently with new uraninite standards. In addition there is still an uncertainty of some 3 % in the exact ratio between the uranium and radium in minerals. For accurate work, wherever possible, the γ -ray method is to be preferred, though in the case of materials suspected to contain mesothorium the emanation method furnishes a very valuable check.

Radioactivity.—The radioactivity of radium itself, free

from the products of its own disintegration, consists of α -rays. In addition there is a feeble and unimportant (β)-radiation, and more recently three types of feeble (γ)-radiation have been detected. In solution the emanation, which is the first disintegration product, escapes freely, but in the solid state it is retained to a greater or less extent, depending upon the nature of the compound. For the sulphate and dry chloride the retention is fairly complete, for the bromide as much as one-half of that produced may escape, whilst from hydroxides, carbonates, and similar compounds it appears to escape most freely. In a sealed tube of glass, however thin, retention is complete. The most penetrating rays come entirely from one of the later products of the emanation (RaC), and therefore the penetrating radiation of a radium preparation varies according to the proportion of the full equilibrium amount of emanation present. A freshly prepared sealed radium preparation attains of this equilibrium amount one-half after four days, three-quarters after eight days, and so on, the equilibrium being practically reached in from three weeks to a month. The sudden removal of the emanation by solution or heating causes no immediate alteration of the penetrating rays, as the emanation itself gives only α -rays. But a gradual decay commences, which is slow for the first half-hour (owing to the existence of the intermediate product RaB), and then is more or less regular; the activity falling continuously to about half-value every half-hour, and the decay being practically complete in three to four hours.

As regards the α -radiation, that due to radium itself is about 18 % of the full equilibrium α -radiation of radium and all the products up to radium C. After removal of the emanation there is a rapid fall in the α -radiation, due to the decay of the α -rays of RaA, which is nearly complete in ten minutes, then a pause for half an hour, and then a more or less exponential decay to the 18 % minimum much at the same rate as for the penetrating rays. When the radium emanation is introduced into an air-tight electroscope the converse of these changes occurs, namely, a rapid rise of activity for ten minutes, and then a more gradual rise, lasting about three hours, to a maximum, followed by the slow decay to half-value every four days

characteristic of the emanation itself. If the latter is at any time blown out and removed, there is again a rapid decay of activity during the first ten minutes, followed by a more gradual one almost to zero in about three hours. The existence of this most characteristic set of changes of radio-activity affords an infallible qualitative test for the presence of radium by means of its emanation in any quantity, however minute.

The measurements of the α -rays afford the only way of following the progress of concentration during the fractionation of a radium-bearing salt, for when freshly prepared from its solution the crystals possess about 18 % of the equilibrium α -activity, but no β - or γ -activity. Mesothorium does not give α -rays, and therefore its presence does not interfere in this case. The difficulties about this kind of measurement centre in the intense ionisation produced by the α -rays from even minute amounts of radium, and the impossibility of cutting it down satisfactorily by screens or by removing the preparation to a distance from the electro-scope. It can be overcome by increasing the capacity of the electro-scope by means of a condenser, but then the danger is that the potential gradient, due to the charge on the leaf, is insufficient to saturate the gas. With a sufficiently high source of potential, a separate ionisation chamber, and a quadrant electrometer many accurate methods can be devised, but these requisites, especially the first, are not always to be found in a chemical laboratory. The escape of emanation from the concentrated radium salts is a very serious difficulty, and it may be necessary to convert the radium into sulphate to minimise this. One mode of procedure in this case would be to introduce uniform films of the radium sulphate of definite area into an air-tight electro-scope, and to exhaust the latter to a definite low pressure, measured by a barometer. At low pressures the ionisation is reduced proportionally to the pressure, and the "saturation" difficulty is avoided. But it would probably be simpler to "degrade" the radium during conversion into sulphate by addition of a known quantity of barium, so as to give a preparation of manageable activity.

Naturally the greatest precautions have to be taken in working with bare radium preparations to avoid contamina-

tion of the measuring instruments. Their introduction into the same room as the instruments is apt to spoil the latter permanently. Not only is there the ordinary contamination due to the escape of emanation and the coating of all the walls and objects of the room with films of radio-lead and polonium, which is a well-recognised danger, and which must be guarded against by carrying on chemical operations with radium as remote as possible from the instrument room, into which only sealed tubes of radium may be taken. But there is also an actual species of volatilisation from bare films of radium exposed in the open air, which possibly is a kind of recoil effect, and which results in the coating of all the objects of the room with particles of radium itself.⁷² Once this has occurred, delicate instruments such as electroscopes are useless, and must be replaced by less sensitive ones, which, as already explained, are less simple, as they require the use of high potentials, with separate ionisation chambers and measuring instruments. But if contamination is avoided, most if not all of the instruments required, except the reading microscope of the electroscope, can be and are better made with one's own hands.

RADIUM EMANATION

Atomic weight—222.

Density—111 (H=1).

Period of average life—5.55 days.

Period of half-change—3.85 days.

Radioactive constant—0.00751 (hour)⁻¹.

Radiation— α -rays.

Range of α -rays—3.94 cm. of air.

Chemical analogue—Homologue of xenon.

Parent—Radium.

Disintegration product—Radium A.

The radium emanation, on account of its comparatively long period and the ease with which it may be separated from inactive material and from its parent and products, and the large quantities of its parent that have been separated in the pure state, is by far the most completely investigated of the shorter-lived radio-elements. Chemically, all three emanations are distinguished by that complete absence

of combining power characteristic of the gases helium, neon, argon, krypton, xenon, so that they are not chemically absorbed by any reagent. On the other hand, they are all condensed at liquid-air temperature. In the case of the radium emanation, the condensation and volatilisation occur with remarkable sharpness usually between the temperature of -152° and -154° C., but the phenomenon depends somewhat on the conditions and the quantity of emanation.

If a radium solution is kept for some time in a closed flask the emanation steadily accumulates with time, half of the equilibrium amount forming in four days, three-quarters in eight days, and so on, equilibrium being practically reached in three or four weeks. In addition, hydrogen and oxygen are formed from the solution by the radioactive decomposition of the water. On exploding the gases, a slight excess of hydrogen remains with the emanation. This may be admitted to a vacuous bulb immersed in liquid air. The emanation is condensed, and the hydrogen, together with any helium produced from the emanation, can be pumped away. As the emanation in presence of oxygen exerts a powerful oxidising action on organic compounds, for example, tap grease, the emanation so obtained is usually contaminated with oxides of carbon, and may be purified by long contact with freshly ignited lime or baryta. The volume of emanation, at N.T.P., in equilibrium with 1 gram of radium, is almost exactly 0.62 cub. mm.⁷³ This latter value is the theoretical volume on the assumption that the emanation molecule consists of single atoms, so that the agreement between the theory and experiment directly proves the monatomic character of the molecule. The spectrum consists of a large number of bright lines, and is similar to that of xenon, its nearest analogue.⁷⁴ On account of its relationship with the argon group the name "niton" has been suggested, but has not been generally adopted on account of the obvious advantages of its original name in expressing its radioactive relationships and of the disadvantage in proposing a new name for one only of the three emanations known. Its atomic weight has been recently determined from its gas-density, both by Bunsen's method, using its rate of effusion through a perforation in a plate,⁷⁵ and directly by weighing on a micro-balance of quartz sensitive to a

millionth of a milligram.⁷⁶ Although in small quantities its condensation and volatilisation are remarkably sharp, in larger quantities it possesses an appreciable vapour pressure, the curve of which has been determined, from the critical temperature 104.5° and pressure 47,450 mm. to its freezing-point, -71° , at which its vapour pressure is 500 mm. The liquid emanation under the microscope is described as colourless and transparent, whereas the solid is opaque, and glows with great brilliancy like a tiny arc-lamp with steel-blue colour, which changes to brilliant orange-red at a lower temperature.⁷⁷

The production of helium in spectroscopic quantity was first observed for the radium emanation on about 30 mgm. of radium bromide.⁷⁸ In later experiments the emanation has been enclosed in a very thin-walled capillary tube, thin enough to allow the α -rays to pass through, but perfectly impervious to ordinary helium. The production of helium was detected outside the tube, proving directly the identity of the α -particles and helium. The α -particles have sufficient velocity to penetrate into ordinary materials to a depth of a few hundredths of a millimetre, and the helium produced from the emanation is largely driven into the walls of the containing vessel, and slowly diffuses out again in the course of time.¹²

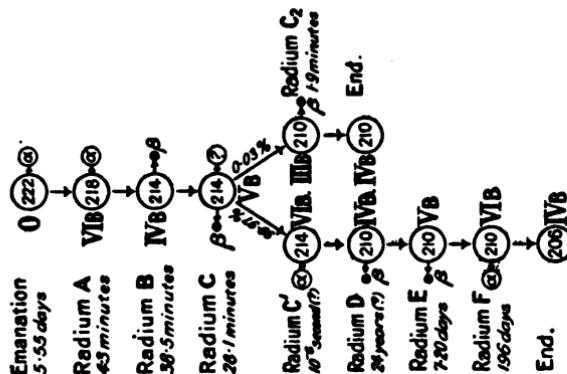
The peculiarities of the radioactivity of the emanation consequent upon the production of the non-volatile "active deposit" have already been fully discussed under the emanation method of estimating radium (p. 97), whilst the differences in the ease with which the emanation escapes from various radium compounds have also been dealt with (pp. 37 and 97).

Cocoanut charcoal has the power of absorbing the emanation at the ordinary temperature, and may be used for this purpose when liquid air is not available.²⁸ The emanation is again given out completely when the charcoal is strongly heated, but it is also evolved quite rapidly at ordinary temperature. If the charcoal that has absorbed emanation is exposed to the open air for a few hours, by far the greater portion of the emanation escapes. Other solid substances, as meerschaum, finely divided metals, and even ordinary metal surfaces have the power of absorbing

the emanation to some extent. This is a possible source of error in certain experiments, for example, when the subsequent activity of metal plates which have been exposed to the emanation is being studied.

The radium emanation is distinctly soluble in water, the coefficient of solubility being about 0.3 at ordinary temperature, and 0.12 at 80°. It is much more soluble than this in all organic liquids, except glycerine. In petroleum and toluene, the solubility coefficients are 9.5 and 11.7 at the ordinary temperature. It is less soluble in salt solutions than in pure water.⁷⁹ Its solubility in fluids is governed by precisely the same laws as those which apply to other gases.

RADIUM "ACTIVE DEPOSIT"



	RaA.	RaB.	RaC.	RaC'.	RaC ₂ .
Estimated atomic weight	218	214	214	214	210
Period of average life (min.)	4.3	38.5	28.1	order of 10^{-8}	1.90
Period of half-change (min.)	3.0	26.7	19.5	„	1.38
Radiation	α	$(\beta) \& (\gamma)$	{ 1st Mode α 2nd Mode $\beta \& \gamma$ }	α	β
Range of α -rays (cm.) of air)	4.5	...	3.9 (calculated)	6.57	...
Absorption coeff. cients	$\mu_{(\beta)} Al = 75$ $\mu_{(\gamma)} Al = 230$ " = 40 " = 0.51	$\mu_{\beta} Al = 13.5$ $\mu_{\gamma} Al = 0.115$ $\mu_{\gamma} Pb = 0.50$
Chemical analogue:—					
Isotopic with Polonium.		Lead.	Bismuth.	Polonium.	Thallium.

The radium "active deposit of rapid change," so called to distinguish it from its products, radium D to radium F, which are more permanent, and are sometimes therefore spoken of as the radium "active deposit of slow change," comprises a group of three successive products, radium A, radium B, and radium C. The latter is believed to disintegrate in two ways. In one a β -ray is first expelled producing radium C', which then expels an α -ray. In the other an α -ray is first expelled, producing radium C₂, which then expels a β -ray. The first member, radium A, is much shorter-lived than the two succeeding members, and gives α -rays on disintegration. In consequence all experiments on radium A must be carried out within a very short time of its production from the emanation. If a negatively charged wire is exposed for a few seconds only in a relatively large quantity of radium emanation, the activity of the wire at first is almost entirely due to the α -rays of radium A, and these decay to a very small value in a few minutes after withdrawal of the wire from the emanation, the activity of the subsequent products formed being, for such short exposures, usually negligible. After twenty to thirty minutes' exposure to the emanation, the quantity of radium A attains equilibrium, and does not further increase. But the amounts of radium B and C on the wire go on increasing with the time of exposure up to three or four hours. Obviously the shorter the time of exposure the purer is the radium A deposited. Conversely with a wire which has been exposed any length of time to the emanation, no radium A remains after twenty to thirty minutes from withdrawal, the activity at this stage being due to radium B and C. Hence, without chemical treatment, radium A alone or radium B and C together may be obtained at will by suitable choice of the time of exposure to the emanation and of the time elapsing after withdrawal.

The decay of the active deposit after withdrawal from the emanation naturally varies very much according to the time of exposure. There is always a rapid initial decay of the α -rays due to the change of radium A, which is the more marked the shorter the time of exposure to the emanation. This is followed by a period of very little change for about half an hour, as the decay of radium C is more or less

balanced by its production from the radium B. Then follows a continuous decay to nearly zero in about three or four hours, with a half-period intermediate between that of radium B and radium C. The most penetrating γ -rays are a measure of the quantity of radium C alone present, and therefore do not show any initial decay due to radium A, but rather an initial increase, or lag in the rate of decay, according to the time of exposure, as radium C is being produced by the changes of radium A and B.

On heating the wire carrying the active deposit in air, the volatility of the products is very different.⁸⁰ Radium B is strongly volatilised at about 600° , whilst radium C requires a much higher temperature, and does not commence to volatilise till about 1100° . As regards radium A, its true volatilisation temperature is probably between 800° and 900° , for if a wire, maintained at the latter temperature, is exposed to the emanation it does not become active, however charged.⁸¹ The following volatilisation points are given: radium A, 900° ; radium B, 600° ; radium C, 1100° . As already explained (p. 41), these volatilisation temperatures are quite different in hydrogen.⁸⁰ A practical method for obtaining radium C by itself is to allow the radium A on the wire to decay, and then to expose the wire for some minutes to a temperature somewhat above 630° . Radium B distils away, leaving radium C on the wire, the total activity of which then decays exponentially with the half-period of 19.5 minutes. The other method mostly employed for this purpose is to dissolve the active deposit off the wire in boiling dilute hydrochloric acid, and to shake up the solution with finely divided metallic nickel, or to plunge into it a copper or nickel plate. Radium C alone deposits on the metal, leaving radium B in solution.⁸² The radium B, so left, of course immediately starts to produce a fresh amount of radium C by its own change. Itself it produces only (β)- and (γ)-radiation, but it is characterised by its power of generating with the lapse of time the powerful α -, β -, and γ -radiation of radium C. Similarly, by electrolysis of the solution of the active deposit with a feeble current and large electrodes, radium C alone is deposited on the cathode.

Radium B may readily be obtained from radium A by recoil.⁸³ At one time it was thought that radium B was

volatile at the ordinary temperature, but its "volatility" is confined to the nascent state, that is, to the radium B actually being produced from radium A. After all the latter has disappeared, the radium B does not volatilise below a red-heat. At ordinary temperatures with radium A present, the radium B at the moment of its formation is largely projected from the plate or wire coated with the active deposit, by recoil of the radium B molecule when the radium A α -particle is expelled. The collection of such recoiled products on surfaces is most favourable in a vacuum, with the receiving surface kept negatively charged.

The isotopism of the A, B, and C members with polonium, lead and bismuth respectively, which has been established by direct experiment on the chemical character of these radio-elements,⁸⁴ renders it unnecessary to discuss in further detail their chemical reactions. In presence of these elements their chemistry can be foretold to the minutest detail, by proxy. In the radio-chemically pure state they may be used to extend our knowledge to these three elements, respectively, in quantities almost inconceivably less than can be studied by chemical analysis.

Radium C₂.—The branching of the disintegration series at the C member is discussed in Part II, p. 24. Owing to the excessively minute proportion of radium C₂, for most purposes this branch may be entirely neglected. Radium C₂ is obtained from radium C by recoil, but comparatively large quantities have to be worked with to put it in evidence.⁸⁴ This recoil is also the sole indication we yet have of the α -rays which are supposed to accompany its production from radium C. Its period is fairly accurately known, but the character of its radiation, beyond the fact that it closely resembles that of radium C itself, has not yet been analysed in detail. It is not known whether it gives a γ - in addition to the β -radiation. Its theoretical isotopism with thallium has not yet been tested.

Radium C.—If we neglect radium C₂, and regard radium C from a purely practical point of view, it appears to be a homogeneous radio-element, with half-period of 19.5 minutes, giving α -, β - and γ -rays, all three types being the most penetrating and powerful known in the whole uranium series. Cursorily examined, its radiation appears to decay

completely, each type at the same rate, but a more careful investigation with powerful preparations puts in evidence a residual activity, due to radium D and its products, which at first steadily increases with lapse of time. By careful arrangement nearly the full theoretical 50 % of this radium D may be obtained from radium C by recoil, which is proof that it is the product of the α -ray change.

Radium C'.—Application of the Geiger-Nuttall relation shows that the α -rays must be derived from a change of very great rapidity, and this, the recoil evidence and the fact that the α -rays decay always at the same rate as the β - and γ -rays, leads to the scheme adopted, in which the hypothetical transitory α -ray giving member "radium C'" intervenes in the direct line between radium C and D. Naturally its theoretical isotopism with polonium cannot be experimentally tested, owing to its fleeting existence, but there is no reason to doubt this application of the rules. It is a matter of considerable interest that the complete chemical character of an element, existing on the average probably not more than a millionth of a second, can be so completely predicted.

RADIO-LEAD OR RADIUM D

Estimated atomic weight—210.

Period of average life—24 years (?).

Radiation— (β) - and (γ) -rays.

Absorption coefficients— $\mu_{(\beta)}\text{Al} = 1.30$.

$\mu_{(\gamma)}\text{Al} = 45; 0.99.$

Chemical analogue—Isotope of lead.

Parent—Radium C'.

Disintegration product—Radium E.

This element has not yet been separated or concentrated from lead, which, so far as is known, it resembles perfectly in all its chemical reactions. As lead is an invariable constituent of all uranium minerals, and in all except autunite is present in notable quantity, the lead separated from such minerals always contains the radio-lead associated with the uranium. Conversely, common commercial lead contains traces of the element which causes it to be distinctly more

radioactive than most other metals. For making instruments, a very old lead (such as from an old roof) should if possible be employed, as in this the radioactive constituent will largely have decayed. Although itself giving only a non-penetrating (β)- and (γ)-radiation, its product, radium E, gives β -rays, and as the latter is of short period, the β -radiation is rapidly produced. More slowly an α -radiation makes its appearance, due to the production of radium F (polonium). In consequence the lead separated from uranium minerals shows, a few days after separation, a marked β -activity, and in the course of a few months an α -activity also. By purification the radio-lead is very easily obtained again inactive, but only to regenerate its activity in course of time. Owing to the large amount of lead in uranium minerals, radium D as yet is technically of little value, for no means of concentrating the activity exists. If it could be concentrated it would for many purposes be as valuable as radium itself.

Another source of radio-lead, however, is old radium. The period of radio-lead, although long, is still short enough to cause its production from radium to be easily detectable. After the decay of the active deposit of radium is complete, an extremely feeble activity is left, which then increases, the β -radiation for a few weeks and the α -radiation for a couple of years. This is due to radium D, which, after formation, produces first radium E and then radium F. In old radium preparations which have been kept in the solid state, or under conditions where the emanation is retained, the radio-lead steadily accumulates, and may be separated with the radium, from the polonium and radium E, by precipitation with sulphuric acid. From the radium it may be separated by adding a little lead and then separating it by any convenient method.

However, if a preparation of radio-lead is required as concentrated and pure as possible, the simplest method of procedure is to remove the emanation periodically from a radium solution kept in an air-tight vessel, and to introduce it into a closed glass flask. As the emanation decays, radio-lead is formed and accumulates as an invisible film on the walls of the flask. Tubes that have contained extremely concentrated emanation from large quantities of radium

show a sub-metallic deposit on the glass, which perhaps may be due to visible amounts of pure radio-lead and its products.

Recent researches have shown that it is radium D which is responsible for almost all of the soft (γ)-radiation which was at one time assigned to radium E.⁸⁵

RADIUM E

Estimated atomic weight—210.

Period of average life—7.2 days.

Period of half-change—5.0 days.

Radiation— β -rays.

Absorption coefficient— $\mu_{\beta}\text{Al} = 43.3$.

Chemical analogue—Isotope of bismuth.

Parent—Radium D.

Disintegration period—Polonium (Radium F).

This short-lived member gives out β -rays, and stands between a long-lived element producing only (β)-rays and a less long-lived α -ray producing element. It is therefore completely analogous to mesothorium 2 of the thorium series. At one time it was regarded as complex, consisting of a rayless element, radium E₁, of half-period 6.5 days, which produced the β -ray giving element, radium E₂, with half-period 4.8 days, but later evidence has shown that it is single and in its chemical behaviour is the isotope of bismuth. On electrolysing a solution of acetate of lead, containing radio-lead and its products, with gradually increasing current densities, the polonium is first deposited on the cathode (at 4 micro-amperes per cm.²), then polonium and radium E separate (at 10 micro-amperes), while with heavier currents all the products are deposited. This is an example of von Lerch's partially true generalisation, that the successive products of a disintegration series become electro-chemically more "noble," and are deposited the more easily as we pass through the series. They also, as a general rule, become more volatile and more readily soluble in acids.

The β -rays of radium E are absorbed exponentially by aluminium, the coefficient of absorption being 43.3. This is about three times greater than that of the β -rays of uranium

X, so that the radiation is comparatively feebly penetrating. The γ -rays accompanying the β -rays are extremely feeble, and do not amount to more than 2 %, relatively to the β -rays, of those given by radium D. But they appear to have identical absorption coefficients, and are theoretically of great interest on that account.⁸⁵ The γ -rays of radium D and E together do not interfere at all with γ -ray measurements of the strength of minerals and of radium preparations, when the rays are, as is customary, first passed through 1 cm. of lead. As the β -radiation of radium E decays, an α -radiation due to radium F makes its appearance, but as the period of the latter is long compared with that of its parent, the α -radiation so produced is not very pronounced. In turn, of course, it decays completely with the period of radium F.

POLONIUM. (Radium F)

Estimated atomic weight—210.

Period of average life—196 days.

Period of half-change—136 days.

Radiation— α - and (γ)-rays.

Range of α -rays—3.58 cm. of air.

Absorption coefficient— $\mu_{(\gamma)} Al = 585$.

Chemical analogues—Homologue of tellurium, allied to bismuth.

Parent—Radium E.

Disintegration product—Unknown, probably lead.

Owing to its period, being intermediate between the long-lived and short-lived radio-elements, two possible sources of polonium are available. It may be obtained from uranium minerals, being separated analytically with sulphuretted hydrogen in Group II, and resembling bismuth most closely of the members of this group. Or, it may be obtained from old preparations of radio-lead or radium. The quantity of polonium in radio-lead increases to a maximum, which is reached in about two years, and then steadily diminishes as the parent decays. In old radium, the emanation of which is not allowed to escape, the quantity of polonium must steadily increase for thirty years or longer, and owing to the intermediate existence of radio-lead, a comparatively long-lived member, the produc-

tion for the first ten years or more is small. Since radio-lead is a by-product of no direct value, it should furnish the cheapest and most convenient source of polonium. On precipitation with sulphuric acid the radium E and radium F remain in the solution, and after a few weeks the former has completely disintegrated, leaving the latter by itself. On a large scale, the hot saturated solution of the radio-lead nitrate may be crystallised and the polonium concentrated in the mother liquor. This, after the addition of a little bismuth to hinder the deposition of radium E, is electrolysed between platinum electrodes with a cathode potential not exceeding 0.08 volt, or a current strength not exceeding 0.16 milliamperes per square centimetre. The polonium may be removed from the cathode by volatilisation at 1000° and condensed on the surface desired, which is preferably made of palladium or platinum.³⁸

If the ordinary radium-containing residues of pitch-blende are digested with hydrochloric acid, part of the contained polonium is dissolved, and may be precipitated with sulphuretted hydrogen. From the acid solutions obtained in the working of the residues for radium, polonium may also be similarly obtained. About 3 kilograms of bismuth oxychloride are obtained from 1 ton of Joachimsthal pitch-blende. The polonium may be separated (1) by fractional precipitation from solutions made very acid with hydrochloric acid, the polonium being enriched in the precipitate; (2) by sublimation *in vacuo*, the polonium being the more volatile; (3) by fractional precipitation of the basic nitrate with water, the precipitate being enriched (Mme. Curie). Very elegant methods have been devised by Marckwald, who proposed the name *Radio-Tellurium* for the substance before its identity with polonium was established by observations on its period. By immersing a plate of bismuth, silver, copper, &c., in the hydrochloric acid solution, the polonium is practically completely precipitated. In the same solution stannous chloride produces a small black precipitate consisting mainly of tellurium and containing nearly all the polonium. If this is dissolved in not too acid solution and hydrazin hydrate added, the tellurium is precipitated and the polonium remains dissolved, and may be precipitated by stannous chloride. In this way 4 milligrams

were obtained from 2 tons of pitch-blende. Naturally it was intensely radioactive. A hundredth of a milligram sufficed to render a zinc sulphide screen plainly visible in the dark to a large audience.⁸⁶ The theoretical quantity of polonium in minerals is 1 milligram for every 14 tons of uranium (element), assuming that no radium emanation escapes from the mineral. Latterly Mme. Curie, separating the polonium from several tons of pitch-blende, obtained as final product 2 milligrams, which were estimated to consist of polonium to the extent of 5 %. It showed several new lines in its spectrum, which are being periodically examined as the polonium disintegrates, to see if they disappear and give place to the lines of lead.⁸⁷ But difficulties were encountered with the lead derived from the paint off the walls of the room, and the series of experiments has had to be recommenced.

The exponential decay of the activity of polonium is perfectly regular and complete, about one-half per cent. of the activity decaying daily, the half-value being reached in twenty weeks. Like ionium, it gives only α -rays of comparatively low range, no effect being produced through a single thin sheet of paper, even with the most intense preparation. The (γ)-rays, recently put in evidence, are only just detectable by delicate instruments from very active preparations.⁸⁸ It has proved an extremely useful radioactive substance, but for most purposes ionium would now be preferred on account of its greater permanence. The product of polonium should be isotopic with lead, and have an atomic weight of 206, whilst the product of radium C₂ should also be isotopic with lead, and have the atomic weight 210.

THORIUM (Th)



Atomic weight—232.4.

Period of average life— 2.6×10^{10} years (?).

Radiation— α -rays.

Range of α -rays—2.58 (?) cm. of air.

Disintegration product—Mesothorium I.

The chief sources of thorium at the present time are (1) monazite sand from Brazil, N. and S. Carolina, U.S.A., and the state of Travancore, India, from which practically all the thorium used technically is obtained ; it consists of 60 or 70 per cent. of monazite in fine grains with other sands, composed of granite, rutile, zircon, magnetic and titaniferous iron-stone, not attacked by acids ; (2) thorianite, a rare mineral from Ceylon, which contains as much as 60 to 70 per cent. of ThO_2 in a form soluble in moderately strong nitric acid and from 10 to 20 per cent. of U_3O_8 . Formerly thorium was obtained principally from the silicates, thorite and organoite, found in Norway, but these sources are exhausted for technical purposes. Monazite is mainly a phosphate of the rare earths, cerium, lanthanum, præsodymium, and neodymium, with variable amounts of thorium. Usually the commercial sand contains 4 to 5 per cent. of ThO_2 , having been concentrated by washing to this percentage. In addition, small quantities of iron oxide, lime, alumina, and silica are present.

In the first stage of the technical treatment of this sand, it is heated with twice its weight of sulphuric acid. The cold mass is dissolved in water, and left to settle. The solution is then fractionally precipitated with magnesia, the

thorium being concentrated mainly in the first fractions precipitated. The commonest and most useful reagent for precipitating the rare earths from a solution containing common earths such as alumina, iron, &c., is oxalic acid. Now thorium oxalate is of all the rare-earth oxalates the least soluble in acids, so that by working in fairly strong nitric acid solution thorium oxalate may often be precipitated and separated at least partially from the other rare earths and from calcium. The same is true of the rare-earth phosphates, that of thorium being one of the most insoluble in dilute acids. On the same principle, thorium is often precipitated by weak bases, such as the substituted ammonias, for example, dimethylamine, while zirconium, &c., remain dissolved. The potassium salt of hydrazoic acid, KN_3 , precipitates thorium hydroxide only from mixtures of thorium and cerium on boiling. Another reagent that may be employed is meta-nitro-benzoic acid. The same separation may be effected by means of sodium thiosulphate on boiling, thorium alone being separated, as hydroxide. This ready hydrolysis of weak thorium salts is characteristic of the element. The oxalates of thorium and zirconium alone of the rare earths are soluble in ammonium oxalate, and on strongly acidifying the solution the former alone is reprecipitated. The solution of the oxalate of thorium and its conversion into soluble salts may be effected by means of concentrated ammonium or sodium carbonate and precipitation of the concentrated solution as thorium hydroxide with strong ammonium or sodium hydrate. Or it may be dissolved by digesting with *fuming* nitric acid, an operation of great utility in analysis. Thorium is distinguished from the yttrium group of the rare earths by its power of forming a double sulphate with potassium sulphate, insoluble in excess of the latter reagent, and so may be separated from a mixture of the sulphates by saturating the solution with potassium sulphate. One of the reactions most relied upon in the purification of thorium from rare earths, in analysis, is the precipitation of the peroxide by hydrogen peroxide. A 10% solution of the latter is added to the dilute neutral, or only faintly acid solution containing thorium at 60° . The precipitate obtained can be redissolved in acid, neutralised, and again precipitated as often as required. This reaction serves

to separate thorium from actinium and its isotope, mesothorium 2.

Alike in the old, now obsolete, as in the present technical methods of purifying thorium, the peculiar solubility relations of thorium sulphate in water have been largely applied. The older method consisted in volatilising the excess of sulphuric acid from the material being treated, and in dissolving the anhydrous sulphates in ice-cold water—a tedious operation—and in heating the solution till the hydrated thorium sulphate was precipitated. The latter was then dehydrated at 300° to 400° , and the process repeated. In present practice the sulphuric acid is always kept in great excess in the initial treatment of the mineral, but the sulphate method may be employed at the final stage of manufacture as follows. The thorium hydroxide is dissolved in hydrochloric acid, so that the solution contains not more than 30 % ThO_2 , and sulphuric acid is added to the extent of a half per cent. more than the equivalent quantity, the temperature being kept low, and in any case below 40° as a maximum. Under these conditions the hydrate $\text{Th}(\text{SO}_4)_2 \cdot 8\text{H}_2\text{O}$ is precipitated, departure from the conditions causing the separation of the tetrahydrate, which is in every way less easily manipulated. The precipitated sulphate is reconverted into hydroxide, and the process repeated as often as necessary to remove all impurities.⁸⁹

Thorium forms a curious compound with acetyl acetone, $\text{Th}(\text{C}_5\text{H}_7\text{O}_2)_4$, which is soluble in chloroform and alcohol, and can be distilled in a vacuum, and so can advantageously be employed for the purification and separation of the element.

It may be mentioned that in the fusion of refractory minerals, for example, with sodium carbonate, the thorium, if present, is converted into the highly insoluble oxide, ThO_2 , and its presence is apt to be overlooked.

Thanks largely to the thorium industry, in which a product unusually pure is essential, there exists, therefore, a great variety of exceedingly good and sharp methods for the separation and purification of thorium, and it must be understood that ionium, if present, and radiothorium always remain unseparated from thorium in these processes as far as they have been examined.

A glance at the disintegration series above shows that radiothorium and its products are responsible for by far the

larger part of the radioactivity of the whole series, just as radium is for that of the uranium series. The three bodies preceding radiothorium in the series yield only a very small proportion of the α -rays, and about half of the β - and γ -rays. Thorium, free from radiothorium, has not yet been prepared, and although this is now theoretically possible, by the repeated removal of the mesothorium as fast as it forms over a period long enough to allow the radiothorium present to disintegrate completely, the operation would require many years. For this reason, and also on account of the ionium always present from the uranium of the original mineral, it is difficult to examine the α -rays of thorium itself. The range of the α -rays, from a thorium preparation in which the radiothorium has largely decayed, is, however, distinctly less than that of the α -rays of ionium.¹⁴

The non-separability of radiothorium and thorium results in all thorium preparations in the ordinary state yielding α -rays of the same order of intensity as that of uranium preparations, but more penetrating, and β -rays about one-tenth as intense, and less penetrating than those of uranium. The γ -rays, like the β -rays, are relatively feeble, but those of thorium C are the most penetrating known, while those of mesothorium 2 are only slightly less penetrating than the radium C γ -rays. Freshly prepared from minerals, and retaining therefore the full equilibrium amount of radiothorium, the activity of thorium salts attains a maximum after one month (due to the accumulation of thorium X), and then steadily decays. Thorium X and mesothorium 1 resemble radium chemically, and are always separated completely in the processes of manufacture. The absence of the mesothorium initially causes the α -rays due to radiothorium and its products to decay to a minimum, which is about one-half of the maximum value, in about four and a half years, when further decay is just balanced by fresh radiothorium resulting from the now partially regenerated mesothorium. The activity must then increase again for several decades until the maximum value is regained. Thus the radioactivity is a complex function of the age of the thorium preparation, and for this reason alone thorium is entirely unsuited for use in the preparation of radioactive standards.

But in another respect the radioactivity of this element is quite different from that of uranium. All thorium preparations give out, according to their nature, more or less of the thorium emanation, the volatile product of thorium X with period of half-change of about one minute. If the electro-scope is air-tight, this emanation goes on accumulating for some ten minutes after a thorium preparation is placed inside, so that the activity on this account rises over this period, but may be reduced again to its first value by blowing out the air of the instrument. The proportion due to the emanation is the greater the greater the mass of the preparation, whereas the proportion due to the α -rays of the solid substance is fixed only by its surface. In consequence, the effect of the emanation is more marked with thick than with thin layers. After being exposed to the emanation for some time, the inside walls of the electro-scope become radioactive through the "active deposit," which, once formed, takes some days completely to decay.

Commercial thorium oxide has an emanating power about one-third that of the hydroxide, but by ignition the emanating power is permanently reduced, the more the higher the temperature employed, until it reaches a limit at about one-tenth of that of unignited oxide. Solid thorium nitrate has even less emanating power than this. In these cases the molecules of emanation diffuse out of the solid so slowly that the vast majority disintegrate within the solid itself and never escape. Naturally the radioactivity of the solid non-emanating compounds is higher on this account than that of those from which the emanation escapes easily. On dissolving these preparations the differences in their emanating power disappear.

MESOTHORIUM 1

Estimated atomic weight—228.

Period of average life—7.9 years.

Period of half-change—5.5 years.

Radiation—Rayless.

Chemical analogue—Isotope of radium.

Parent—Thorium.

Disintegration product—Mesothorium 2.

This important substance was discovered some years

ago,⁹⁰ but its chemistry and method of preparation were, for some time, technical secrets. Owing to the enormous quantity of thorium required for the gas-mantle industry, in which mesothorium is a by-product, and to the growing scarcity of uranium minerals, mesothorium, in spite of its comparatively short period of average life, is being very largely manufactured as a substitute for radium. Although itself rayless, its first product, which is short-lived and therefore rapidly formed after it has been separated, gives a powerful β - and γ -radiation. Owing to the subsequent production of radiothorium and its products, mesothorium preparations acquire an α -radiation with time and the β - and γ -radiation is augmented. A maximum is reached in 4.6 years, when the β - and γ -radiation should be about twice that due to mesothorium 2 alone, and the total radioactivity should represent considerably more than one-half of the activity of the thorium in the mineral from which it was derived. After that time the activity, so far as it is due to mesothorium, will decay exponentially to zero, the half-value being reached in 5.5 years, or about ten years from preparation.

The chemistry of mesothorium I can, like that of ionium, radiothorium, &c., be accurately described in a sentence. It is absolutely identical in chemical nature with radium, and cannot be separated therefrom.⁹¹ In consequence, all radium separated from uranium minerals containing thorium, contains also the mesothorium in the mineral, and all preparations of the latter substance contain the radium present in the mineral from which they are derived. For a mineral containing equal proportions of uranium and thorium the proportion of the γ -rays, which are the ones usually used for measurement, contributed by the radium is some five or six times as great as that due to the mesothorium, when measured through 1 cm. of lead. Fractional crystallisation of the chlorides does not effect the slightest change in the ratio of the two active constituents. The methods employed in the extraction of radium from the residues of pitch-blende may be suitably adapted to the working up of the residues from monazite sand. A little barium sulphate may be added to the monazite sand during its treatment with sulphuric acid, and the mesothorium is then completely separated with

the insoluble material left after treatment of the product with water.

The period of mesothorium is several hundred times shorter than that of radium, so that in a preparation having its activity equally distributed between the two constituents, the mass of the chemically identical radium must be many hundred times that of the mesothorium. This fact seems to interpose an almost impenetrable barrier to the further study of the spectrum, atomic weight, &c., of the element. Even when prepared from a mineral like Ceylon thorite, which has only a very small proportion of uranium, the radium must exceed the mesothorium in absolute quantity, though its radioactivity might be quite negligible by comparison. The preparations prepared technically from monazite may be fractionated till free from inactive matter, and then are stated to be four times as active as pure radium compounds, the activity due to the mesothorium being three times as great as that due to the radium. The composition of such preparations is estimated as 1 % mesothorium to 99 % radium, by weight.⁹²

Mesothorium 1 shares with actinium the distinction of being the only radio-element known in the change of which no radiation whatever has yet been detected. Itself in Group II and its product in Group III, it obeys the rule for a β -ray change, and it is most probable that in its change a β -ray is expelled, too feeble yet to have been detected.

MESOTHORIUM 2

Estimated atomic weight—228.

Period of average life—8.9 hours.

Period of half-change—6.2 hours.

Radiation— β -, (γ)- and γ -rays.

Absorption coefficients— μ_{β} Al from 20.2 to 38.5.

$\mu_{\gamma}Al=26.$

$\mu_{\gamma}Al=0.116.$ }

$\mu_{\gamma}Pb=0.62.$ }

Chemical analogue—Isotope of actinium.

Parent—Mesothorium 1.

Disintegration product—Radiothorium.

Mesothorium 1 behaves like an alkaline earth, whilst mesothorium 2 behaves like a rare earth. The latter is in

consequence readily separated from the former by adding ammonia to the solution. A trace of some other inactive material precipitable by ammonia must be present, naturally, to serve as a nucleus in the filtration of the precipitate, and a small trace of zirconium is usually employed. The zirconium brings down also any radiothorium present.⁹³ However, by repeating the process at an interval, say, of one or two days, in which the mesothorium 2 is to a great extent regenerated, the first precipitate alone contains much radiothorium, the mesothorium 2 regenerated in the interval being under these circumstances the more free from radiothorium the shorter the interval. But since radiothorium gives α -rays, whereas the mesothorium 2 gives only β -rays, some α -radiation is always initially shown by the preparations, and for this reason the growth of radiothorium from mesothorium 2 is difficult directly to prove. The period of the former being many thousand times greater than that of the latter, the *growth* of α -rays due to radiothorium is very small. A fuller examination of its chemical character revealed the fact that it is chemically non-separable from or isotopic with actinium, and may be separated, therefore, from thorium by precipitating the latter, in neutral solution, either with meta-nitro-benzoic acid, potassium hydrazoate, or hydrogen peroxide. In this way mesothorium 2 has now been obtained in a pure condition, initially almost free from α -activity. It has been established that the growth of α -activity from it, as its β - and γ -activity decays, proceeds according to the theoretical assumption that radiothorium is the direct product of the change.⁹⁴ Although not yet prepared absolutely free from α -rays initially, these appear to come from the last unremovable traces of thorium C and not from the mesothorium 2 itself.

The β -rays of mesothorium 2 decay regularly with the period given, the decay being practically complete in two or three days. The β -rays are of moderate penetrating power, but are not absorbed exponentially, the absorption coefficient for aluminium increasing from 20.2 to 38.5 [cm.]⁻¹ as absorption proceeds. The γ -rays are, relatively to the β -rays, about one-half as powerful as those of radium, and are rather less penetrating, especially in the case of lead. For other metals the difference is not so marked. In this

the γ -rays resemble rather than those of uranium X. A careful comparison of the absorption of the γ -rays through lead with those from pure radium will reveal the contamination of radium by mesothorium without the necessity of opening the tube containing the preparation.⁹⁵

RADIOThorIUM

Estimated atomic weight—228.

Period of average life—1063 days (2.91 years).

Period of half-change—737 days (2.02 years).

Radiation— α -rays.

Range of α -rays—3.67 cm. of air.

Chemical analogue—Isotope of thorium.

Parent—Mesothorium 2.

Disintegration product—Thorium X.

This radio-element, which resembles perfectly its original parent in chemical nature, would, like the isotope of uranium, have remained experimentally unknowable but for the relatively short life of the intermediate substance mesothorium. The latter can easily be separated both from thorium and from radiothorium. Hence, after separating it from a thorium mineral, mesothorium is left to itself to produce radiothorium, which is then separated by adding to the solution a trace of thorium, or, if that is objectionable, of zirconium, and precipitating this out with ammonia. The precipitate retains the radiothorium and the solution the mesothorium. This is the only known way in which radiothorium can be prepared. The earliest preparations undoubtedly were prepared in this way unwittingly, mesothorium not then having been discovered.⁹⁶ The period has been determined by direct measurements of the rate of decay. When prepared in the manner described, the radiothorium at first retains the mesothorium 2, which decays completely in the course of two or three days. In the meantime thorium X is being produced, which causes an increase of the activity over a period of three or four weeks. The emanating power of the preparation grows with the growth of thorium X. After a month the total activity and emanating power reach a maximum, and then slowly decay to

zero. When required for experiments on the thorium emanation, for which radiothorium is pre-eminently suitable, the thorium hydroxide precipitated from the mesothorium solution should be kept in the moist state and not allowed to dry. With such a preparation all the experiments with the emanation referred to under *actinium* may be repeated with most beautiful and striking results. A puff of air sent through the tube containing the preparation on to the coated surface of a glass zinc sulphide screen, or better, between two such screens placed close together with films inward, gives the most beautiful result, and the decay and reproduction of the emanation with lapse of time can thus be demonstrated easily even to a large audience. From being a phenomenon only to be studied by delicate electric methods, the thorium emanation can now, thanks to the existence of radiothorium, be shown on the same scale as the emanation of radium, and for illustrating the principles of radioactive change is even more suitable on account of its shorter period, and of the longer period of its products, which therefore hardly interfere.

THORIUM X

Estimated atomic weight—224.

Period of average life—5.25 days.

Period of half-change—3.64 days.

Radiation— α - and (β) -rays.

Range of α -rays—4.08 cm. of air.

Chemical analogue—Isotope of radium.

Parent.—Radiothorium.

Disintegration product—Thorium emanation.

The disintegration theory was originally proposed to account for the continuous reproduction of thorium X from thorium salts (due, as we now know, to the always present and inseparable product, radiothorium), and for the production from the thorium X of a whole chain of successive products, commencing with the gaseous emanation. When any thorium compound in solution is precipitated by ammonia, the thorium X, which is an alkaline-earth element like radium, and is responsible for

the whole of the emanating power and the greater part of the radioactivity, is left in solution. Whereas if the precipitant is a carbonate, phosphate, &c., no separation is effected, and the precipitated thorium possesses the same radioactivity and, in solution, the same emanating power as initially. If after precipitation of the thorium with ammonia the filtrate is evaporated to dryness and the ammonium salts volatilised by gentle ignition, a non-volatile residue is obtained, very small in quantity but intensely radioactive, the activity being that of thorium X. If the thorium compound used is, for example, one like thorium nitrate, and has been preserved in the solid state, the emanation is retained, and nearly the full amount of the later products of the "active deposit" thorium B to D will be present. Whereas if a solution of thorium which has been kept for the last two days in an open vessel is used, these products will not be present, at least in their full equilibrium quantity. On precipitation with ammonia the thorium X alone is left in solution, the other products, if present, being precipitated with the thorium hydroxide. The activity of the precipitate thus decays for the first twenty-four hours until the regeneration of thorium X overpowers the decay due to the disappearance of the active deposit. After that time the activity steadily rises and attains equilibrium in three or four weeks. At the minimum the α -rays have about 25 to 30 per cent. of their equilibrium value, whilst the penetrating rays are practically absent, as these come entirely from the "active deposit." The emanating power of a solution is a direct measure of the amount of thorium X, so that if the freshly precipitated thorium hydroxide is free from thorium X, when dissolved and tested for emanating power it will be found to have practically none. Conversely the activity of thorium X, especially after ignition, when the emanation is retained, increases for twenty-four hours and then decays regularly to zero in three or four weeks, according to the exponential law with the period of thorium X.

The emanating power of the solution from which a thorium salt has been precipitated with ammonia is at first the same as that of the original thorium in solution, but this decays exponentially with time to zero, according to the period of thorium X. The emanating power of the

thorium hydroxide meanwhile steadily rises from zero to the equilibrium value. If, instead of ammonia, pyridine, fumaric acid, or meta-nitro-benzoic acid is used as the precipitant, thorium B, as well as thorium X, is left in the solution. As thorium B is by far the longest-lived member of the active deposit group, these reagents are to be recommended when it is desired to prepare quickly thorium hydroxide free from both thorium X and its products. Four precipitations with the last-named reagent, at intervals of two hours, are stated to effect this, and to give a thorium hydroxide of minimum α -activity, no β -activity and no emanating power, the activity of which then increases regularly without the initial decay characteristic of the ordinary precipitate obtained by ammonia.⁹⁷

Since thorium B and thorium C are the isotopes of lead and bismuth, respectively, and meta-nitro-benzoic acid precipitates thorium C, leaving thorium B in solution, the same reagent should effect a similar separation of lead and bismuth. On testing this deduction it was found to be correct, and a separation of these metals may be effected in this way. This is an interesting example of the opposite to the usual case, the determination of new reactions of old elements by proxy, from the reactions of their radioactive isotopes.⁹⁴

The isotopism of thorium X and radium follows from a number of indirect observations rather than from any systematic investigation. The close resemblance was shown first by some experiments on the crystallisation of various salts from saturated solutions containing thorium X. Most salts crystallise leaving the active material in the mother liquor, but the barium salts on crystallisation preserve much the same proportion of the thorium X as the mother liquor.⁹⁸ Of course it should be actually concentrated in the mother liquor, just as radium is, but the point has not yet been specifically investigated.

Out of acid solutions thorium X cannot be separated by electrolysis or by the action of metals, such as copper, zinc, nickel. Only the "active deposit" is separated. But out of alkaline solutions all the active substances may be deposited by these means. Thorium X follows von Lerch's rule, and is less easily deposited, or is electro-

chemically less "noble" than its successive products. It has not been volatilised. The period of thorium X is almost identical with that of the radium emanation, and this is the only case of the kind among the known radio-elements. This, together with its isotopism with radium, leads to some curious results in the separation of thorianite, when the radioactivity is studied by means of the γ -rays. Preparations obtained, for example, by precipitating barium sulphate in the solution may appear to be of constant activity, when what is really taking place is the simultaneous decay of thorium X and the regeneration of radium emanation, leading to a decay of the γ -rays due to thorium C and a growth due to those of radium C.

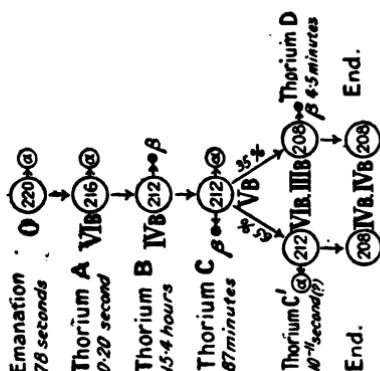
THORIUM EMANATION

Estimated atomic weight—220.
Period of average life—78 seconds.
Period of half-change—54 seconds.
Radioactive constant—0.0128 (sec.)⁻¹.
Radiation— α -rays.
Range of α -rays—4.74 cm. of air (?).
Chemical analogue—Isotope of radium emanation.
Parent—Thorium X.
Disintegration product—Thorium A.

The short period of the thorium emanation and, in consequence, its rapid reproduction after its removal from thorium or thorium X preparations by a current of air, are the features that distinguish it chiefly from the radium emanation. Apart from this the two emanations are very similar, both giving α -rays on disintegration, producing active deposits, being condensed at liquid air temperature and absorbed by charcoal at ordinary temperature but not by chemical reagents. The condensation of the thorium emanation under ordinary circumstances is not so sharp as that of the radium emanation, condensation commencing as high as -120° , and being complete at -155° . Its coefficient of diffusion is similar to that of the radium emanation, being about 0.1, indicating that the molecular weight is high. Direct measurements by the effusion method have given the

molecular weight as between 200 and 210.⁹⁹ As already remarked (p. 37), the emanation escapes from various solid thorium compounds with very different degrees of facility, the solid nitrate and ignited oxide giving it up least, and the carbonate and hydroxides most readily. As will be explained in the next section, the product of the thorium emanation is an excessively short-lived α -ray product, the effects of which in ordinary work are indistinguishable from that of its parent, just as those of radium C' are indistinguishable from those of radium C. Owing to the relatively long period of the other radioactive members of the thorium active deposit, the emanation must be passed for considerable periods through vessels before the active deposit produced on the walls becomes evident. Once produced, the activity continues for two days or more. In the case of the radium emanation the converse is the case. Even when stored for only a few seconds in any vessel, the radium emanation leaves behind a notable active deposit of radium A, the activity of which decays with characteristic rapidity after the emanation is withdrawn. Thorium A decays too rapidly to be distinguishable from the emanation in such experiments. The best source of thorium emanation is a preparation of radiothorium (*q.v.*). The amount of thorium emanation generated by a thorium solution under conditions similar to that for the case of a standard thorium solution can, for the reasons already detailed, only be used as a measure of the thorium in the case of minerals in equilibrium. For minerals the emanation affords a direct measure of the thorium present, which can be far more quickly performed than a chemical estimation. A steady stream of air is passed through the solution into a brass cylinder, containing an axial electrode in an insulated support, connected to the gold-leaf of a separate electroscope. The air stream may be kept constant by means of a T-tube in the circuit dipping beneath water, by allowing part of the air always to blow off through the water, thus preserving a constant head. The leak in the electroscope, when it has become constant, is then compared with that produced by a similar volume of a standard solution of a thorium mineral under identical conditions.

THORIUM "ACTIVE DEPOSIT"



	ThA.	ThB.	ThC.	ThC'.	ThD.
Estimated atomic weight . . .	216	212	212	212	208
Period of average life . . .	0.20 sec.	15.4 hrs.	87 min.	10^{-11} sec. (?)	4.5 min.
Period of half-change . . .	0.14 sec.	10.6 hrs.	60 min.	10^{-11} sec. (?)	3.1 min.
Radiation . . .	α	$(\beta) \& (\gamma)$	{1st Mode α } {2nd Mode β }	α	$\beta \& \gamma$
Range of α -rays (cm. of air) . . .	5.40	...	4.55	8.16	...
Absorption coefficients $\mu_{(\beta)} Al = 110$	$\mu_{\beta} Al = 14.4$ $\mu_{\beta} Al = 21.6$	$\mu_{\gamma} Al = 0.096$
	... $\mu_{(\gamma)} Al = 160$ $\mu_{\gamma} Pb = 0.46$	
	... " = 32	
	... " = 0.36
Chemical analogue:—					
Isotopic with	Polonium.	Lead.	Bismuth.	Polonium.	Thallium.

Thorium A.—The first product of the thorium emanation, thorium A, was the last one to be discovered.¹⁰⁰ It had previously been known that the actinium and thorium emanations emitted their α -particles in pairs, as shown by the appearance of double scintillations on the zinc sulphide screen. In the case of actinium the emission appears simultaneous, whereas in the case of thorium a distinct but very short time interval separates the two members of the pair.¹⁰¹ If, in a dark room, the thorium emanation is allowed to diffuse from a radiothorium preparation into a small cylindrical vessel carrying an axial electrode coated

with zinc sulphide and connected to the negative pole of a battery of 1000 volts, the application of the field is accompanied by the instant brightening of the end of the electrode. On disconnecting the battery the luminosity instantly ceases. The field attracts the negatively charged A atoms, which cause the screen to glow. On breaking the electrical connection, that attracted decays almost instantly. Another way of demonstrating the existence of this excessively short-lived first member of the thorium active deposit is to carry an endless wire, negatively charged, through small holes in ebonite stoppers closing a tube containing a source of thorium emanation, and to drive the wire round by a motor. On applying a zinc sulphide screen, the wire is found to be active while the motor is driving it, and the activity along the moving wire is found to fall off the more quickly the slower the wire is driven. By this or similar devices, the period can be accurately determined. The half-period, $1/7$ th of a second, is the shortest known, except for an analogous much more rapidly decaying product of the actinium emanation.¹⁰² Both are entirely analogous to radium A of the radium active deposit. In all ordinary experiments the effects of thorium A add themselves to those of the emanation, and are indistinguishable from them.

Thorium B.—The second product of the thorium emanation, thorium B, may be considered almost rayless, the very soft (β)-rays it produces not being at all powerful. In consequence, a negatively charged wire exposed for a short time to a very powerful source of thorium emanation, such as can be got by using radiothorium, and then withdrawn, possesses practically no activity a second after withdrawal, but in the course of a few hours a powerful activity due to thorium C and D develops. This activity attains a maximum in 220 minutes, and then decays slowly at first, but, after 5 hours, exponentially to zero with the half-period of 10.6 hours, the decay being practically complete in two or three days. In these changes the α -, β -, and γ -rays vary very nearly uniformly, the period of thorium D, the β - and γ -ray producing body, being too short to enter into consideration. According as the time of exposure to the emanation is increased, the initial rise of the activity becomes

less and less marked, until after several days' exposure, when the whole of the products are initially in equilibrium, the existence of thorium B makes itself felt merely by a temporary lag, over the first five hours after withdrawal, of the decay of the activity. This example illustrates well one point in the theory of successive changes. The course of the curves of activity of the thorium active deposit would be identical in every respect if the periods of thorium B and thorium C were exchanged in the series, that is to say, if the first rayless body had the shorter instead of the longer of the two periods. It is only by separating one of the products in the pure state, and measuring its period of decay, that the choice can be made as to which product has the longer period.¹⁰⁸

The separation of thorium B from thorium C can be effected in various ways. By heating the active wire for a short time to a red-heat, the thorium B alone distils away without any immediate effect on the activity of the wire, which, however, now decays much more rapidly.¹⁰⁴ The sublimate is at first inactive, but acquires an activity reaching a maximum in four hours, and then decaying with the 10.6 hour half-period. The sublimate, therefore, is thorium B. If the wire is heated above 700°, thorium C also volatilises, but heating for a few minutes to 1000° removes all the thorium B and leaves some of the thorium C, which now decays exponentially with the half-period of 55 minutes.

Thorium C.—Thorium C may be removed from a solution of the thorium active deposits in acids by adsorption with animal charcoal, the thorium B remaining in solution. The same is the case when the solution is shaken up with finely divided nickel or exposed to a nickel plate, or when it is electrolysed, thorium C being always the most readily deposited. Zinc, on the other hand, deposits both thorium B and C from a solution, but not thorium X.

The isotopism of thorium B, C, and D with lead, bismuth, and thallium, respectively, has been established by direct experiment.⁸⁴

If we stop our analysis of the active deposit at thorium C, and regard it for convenience as a single product like radium C, it appears to give α -, β -, and γ -rays, all three

types being the most powerful and penetrating in the series. The three types of rays decay completely, and to a cursory examination each type appears to decay at the same rate. But on fuller investigation, although the decay, so far as is known, is complete, slight differences will be observed in the rates of decay for the α -, β -, and γ -radiations. Whereas in the radium series, the powerful β - and γ -radiation comes almost entirely from radium C, thorium C gives only part—the more penetrating part—of the β -rays. But it gives no γ -rays, which come from a successive product, thorium D. Thorium D is not analogous to radium D, but to radium C₂, the difference being that whereas radium C₂ is produced as a minor branch product in very minute quantity, thorium D, though a minor branch product, is produced to the extent of about one-half the thorium C', the major branch product. In the actinium series, on the other hand, actinium D, the analogue of radium C₂ and thorium D, is the sole certain product. If any analogue of the C' members of the other series exists, it is in very minute quantity in the actinium series, and the evidence of its existence is not very convincing.

For long it was known that thorium C gave α -rays of two different ranges, the one set, constituting two-thirds of the whole, having the longest range of any known, 8.16 cm. of air, and the other set, constituting the remaining third, having a range of 4.55 cm.¹⁰⁶ This, from the Geiger-Nuttall relation, leads to the view that the longer rays are derived from a member, termed "thorium C'", of exceedingly short period, estimated at only 10^{-11} second. Then it was found that, by recoil from thorium C, a new member, called thorium D, may be obtained in the pure state, which gives only β - and γ -rays and has a comparatively short period.¹⁰⁶ Later it was found that thorium C gives part of the β -rays, but no γ -rays.

After a careful review of all the evidence, it was concluded that thorium C is disintegrating dually. In the major mode, claiming 65 % of the atoms disintegrating, β -rays are expelled and thorium C' is produced, which changes at once into thorium D, the penultimate member of this branch. In the minor mode, claiming 35 % of the atoms, the low range α -rays result, and the product, so

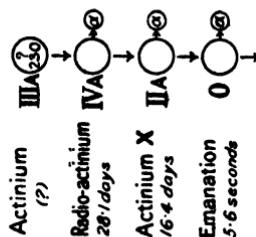
far as appears, is the stable or ultimate member of this branch.¹⁰⁷

The whole scheme depends on the homogeneity of thorium C and the impossibility of separating it into two products, one giving the long and the other the short range α -rays. There is some evidence that such a separation may yet be effected, but, for the present, the scheme may be regarded as pretty firmly established.

Thorium D.—The isotopism of thorium D with thallium was predicted by the Periodic Law generalisation, and immediately verified in a number of characteristic tests. It may be precipitated as platino-cyanide, in presence of potassium or of thallium, and it is precipitated by hydrogen sulphide, in neutral solution, in presence of a member of the second group to act as a nucleus.⁸⁴

If in the separation of thorium C by electrolysis, or shaking with nickel, the operation is accomplished in a few seconds, the thorium C is at first free from thorium D. Its α -rays decay exponentially with the 55 minute interval, whilst its γ -rays are at first zero, but increase to a maximum with the 3.1 minute half-period of thorium D. Thorium D is more easily soluble in acids and is more volatile (being completely volatilised by heating the active wire for 30 seconds in a Bunsen flame) than any of the other products.¹⁰⁸ Thorium D is the last-known member of the series. The decay of the thorium active deposit is regular and complete, no feeble residual activity remaining as in the case of radium.¹⁰⁹ In both branches the ultimate products should be isotopic with lead and have the same atomic weight, 208.4.

ACTINIUM



Atomic weight—Unknown.

Period of average life—Unknown.

Radiation—Rayless.

Parent—Unknown. Probably uranium is the ultimate parent.

Disintegration product—Radio-actinium.

Chemical analogue—Homologue of lanthanum. In basicity between lanthanum and calcium.

As the above headings indicate, actinium is still very little known. Yet its discovery was made by Debierne, in the iron group separated from pitch-blende, very shortly after the discovery of polonium and radium. The total absence of knowledge of its most important radioactive characteristic, its period, which at present is wholly incalculable, alone makes it unique. All that can be said is that the activity of the series appears to be permanent within the few years it has been known, and therefore its period presumably must be at least several times as long as that of polonium. This is perhaps the most important datum in radioactivity still lacking. Next perhaps in importance is the atomic weight, the absence of knowledge of which, of course, extends to the whole series, comprising eight members, of which five emit α -particles. According as the branching of the uranium series occurs at uranium 1 or uranium 2, the calculated atomic weight of actinium itself is either 230 or 226, and there is not yet sufficient evidence to decide between these alternatives. Actinium is a constant constituent of uranium minerals, so far as these have been examined, and this points to uranium being the ultimate parent, but no production of actinium from uranium or

any of its products has as yet been observed. Its peculiarity is its great rarity. The α -activity of uranium minerals is 4.64 times that of the contained uranium. Of this all but 0.28 is contributed by the uranium-radium-polonium series proper, the several activities of the various α -ray products being in agreement with the view that each of the six products expel one α -particle each, per atom disintegrating. Now four or five members of the actinium series expel α -particles, and yet the total proportion of the α -radiation of uranium minerals contributed by the actinium series is estimated as only 0.28 out of this 4.64.¹¹⁰ Were the actinium series in the main uranium-radium-polonium series, its α -activity should be similar to that of the radium series. It seems most probable that one of the members of the uranium series has two ways of disintegrating, the one mode, in which by far the greater proportion of the atoms disintegrate, giving ultimately polonium and the other giving actinium. In consequence of what has been said, it will be clear that actinium must necessarily be excessively scarce even compared with radium. To produce an actinium preparation, which, when in equilibrium with its products, shall have the activity of a given mass of radium in equilibrium, some ten or twelve times as much mineral must be worked up. Moreover, the final complete concentration of actinium from lanthanum, &c., has not yet been successfully accomplished, so that actinium preparations are at once excessively costly, and at the same time disappointing in the intensity of their activity, as compared with radium.

Actinium itself is rayless, and its first product, radio-actinium, has a period of half-change of 19.5 days. As often separated from minerals, free from radio-actinium, actinium preparations are hardly at all active, but the activity and emanating power increase enormously over a period of several months, a behaviour which is characteristic of the substance. It is thus very easy to overlook its presence, and this, coupled with the fact that, as ammonium salts accumulate in an actinium solution, it becomes less and less completely precipitated with ammonia, very special precautions have to be taken in working with actinium not to lose this rare and difficultly won substance altogether. In no case is the maxim, never to be in a hurry to throw

anything away, which ordinary caution imposes on the worker with these materials, so necessary as in working with actinium. Much of that initially won from uranium minerals has been lost irretrievably through insufficient knowledge of these peculiarities.

The whole actinium series bears a remarkably close analogy to that of thorium. The most striking property of actinium preparations is their emanating power, and indeed Giesel gave the name "Emanium" to the substance before the identity of his and Debierne's preparations had been established. Actinium is associated with the rare earths, and usually is prepared mixed with the hydroxides of these substances. These compounds part with their emanation with great ease even in the solid state. In addition, the actinium emanation has an average life-period of only a few seconds, and thus, after removal, very rapidly reforms from its parent. If a preparation of actinium is held over a large zinc sulphide screen in the dark, the emanation streaming away from the preparation illuminates the screen, and the luminosity is blown hither and thither by the slightest current of air. This, at one time, unique property is also shown in even greater degree by suitable preparations of the newer radio-thorium. Actinium, in association with its products, gives powerful α -rays, and preparations 100,000 times as active as uranium oxide in this respect have been described. The β -rays are relatively feebly penetrating. The γ -rays are both feeble in activity and very feebly penetrating, even from very active preparations.

Actinium is easily obtained with iron and rare earths by precipitating barium as sulphate in the acid solution, and this accounts for its presence in pitch-blende residues. In the working up of these, the acid solutions, after removal of polonium with sulphuretted hydrogen, are oxidised and precipitated with ammonia, the actinium being precipitated. The precipitate may be extracted with dilute hydrofluoric acid, the insoluble part, consisting of La, Di, Ce, and Th, retaining most of the actinium. After transformation into chlorides the actinium is precipitated by oxalic acid, and the oxalates, after ignition to oxides, are converted into nitrates, combined with nitrate of magnesium, or of manganese, and fractionally crystallised. The actinium accumulates in the

mother liquor. The rare-earth element most closely associated to actinium is lanthanum, and by this latter fractionation, with the double magnesium nitrate, part of the lanthanum may be removed in the crystals free from actinium. Ionium may be separated by precipitation with sodium thiosulphate, in presence of thorium, the actinium remaining in solution. Auer von Welsbach places actinium between lanthanum and calcium in chemical properties. He observed that in the presence of ammonium salts the precipitation of actinium is far from complete, but it is completely precipitated in presence of manganese from basic solutions as a manganate. This reaction he found of great service in the separation of actinium from pitch-blende residues on a large scale.³⁷

Observations on the penetrating rays of actinium, prepared many years previously, have shown a marked decay of the activity during the last three years, amounting to about 10 %.¹¹ This indicates either that the period of average life of the element is only about thirty years, or that, as in the case of thorium, an intermediate product of long life exists between actinium and radio-actinium. The first explanation makes the continued failure to detect a production of actinium difficult to understand, for this should be easy to do if the period is only thirty years. The second explanation has only analogy to recommend it. On general grounds, since preparations 100,000 times as active as uranium have been prepared, the period cannot be greater than about 1/30,000th of that of uranium, that is about 300,000 years.

RADIO-ACTINIUM

Period of average life—28.1 days.

Period of half-change—19.5 days.

Radiation— α - and (β) -rays.

Range of α -rays—4.36 cm. of air.

Absorption coefficients— $\mu_{(\beta)}\text{Al} = 170$.

$\mu_{(\gamma)}\text{Al} = 25$; 0.190.

Chemical analogue—Isotope of thorium.

Parent—Actinium.

Disintegration product—Actinium X.

Radio-actinium may be separated from its parent and its

products by forming in its solution a fine amorphous precipitate, such as sulphur, by adding a little sodium thiosulphate to the strongly acid solution.¹¹² The actinium and actinium X remain in solution, whilst the radio-actinium is precipitated. The separation, however, was originally described as rather uncertain. The subsequently discovered isotopism of radio-actinium and thorium shows that the uncertainty was probably due to the presence or absence of thorium in minute traces.³⁴ In presence of thorium the separation works perfectly.

When an actinium preparation is treated with dilute hydrochloric acid, a small part usually is undissolved, and this contains a larger proportion of the radio-actinium than the solution. Freshly prepared, the activity of radio-actinium consists entirely of non-penetrating α - and (β)-rays, which increase, in about three weeks, to a maximum of two or three times the initial value, due to the production of actinium X and its products. The penetrating rays and the emanating power of the preparation increase from zero to a maximum in the same time, and then the total activity decays exponentially with the half-period of about twenty days, the decay being practically complete after four months. Actinium itself is often not completely precipitated by ammonia, whereas radio-actinium appears to be more easily precipitated. By fractional precipitation of an actinium solution with ammonia, the radio-actinium is concentrated in the first fractions. The behaviour of the substance is not very definite, except in the presence of thorium. Radio-actinium is exceptional, with radium, in giving both α - and (β)-rays, though in each case the product obeys the rule as though only an α -particle were expelled.

ACTINIUM X

Period of average life—16.4 days.

Period of half-change—11.4 days.

Radiation— α -rays.

Range of α -rays—4.17 cm. of air.

Chemical analogue—Isotope of radium.

Parent—Radio-actinium.

Disintegration product—Actinium emanation.

Actinium X resembles thorium X completely in chemical

nature,⁹⁸ and may be separated from actinium or radio-actinium by precipitation with ammonia.¹¹³ The only difference between this separation and that of thorium X is that the "active deposit" of actinium is separated with the actinium X, but in the ignition of the ammonium salts it is volatilised. The result is therefore similar, so far as the ignited preparation is concerned. Initially it is free from "active deposit," and immediately starts to produce it. The α -rays increase in intensity about one-third, and the β -rays grow from zero to a maximum, in three or four hours, and then the total activity and emanating power decay exponentially with the half-period of ten or eleven days. The actinium hydroxide so obtained is, like the thorium hydroxide precipitated with fumaric or meta-nitro-benzoic acid, initially free from the "active deposit," and in consequence the activity rises from preparation without any initial decay. The α -activity is initially about 28 % of the equilibrium value, which is due entirely to radio-actinium, but owing to the indefiniteness already referred to in the behaviour of the latter substance, it is apt to be separated to some extent from the actinium in the chemical operations for removing actinium X. As in the case of thorium X, the emanating power of a solution is the direct measure of the amount of actinium X present therein at the time of the measurement.

ACTINIUM EMANATION

Period of average life—5.6 seconds.

Period of half-change—3.9 seconds.

Radioactive constant—0.18 (sec.)⁻¹.

Radiation— α -rays.

Range of α -rays—5.40 cm. of air.

Chemical analogue—Isotope of radium emanation.

Parent—Actinium X.

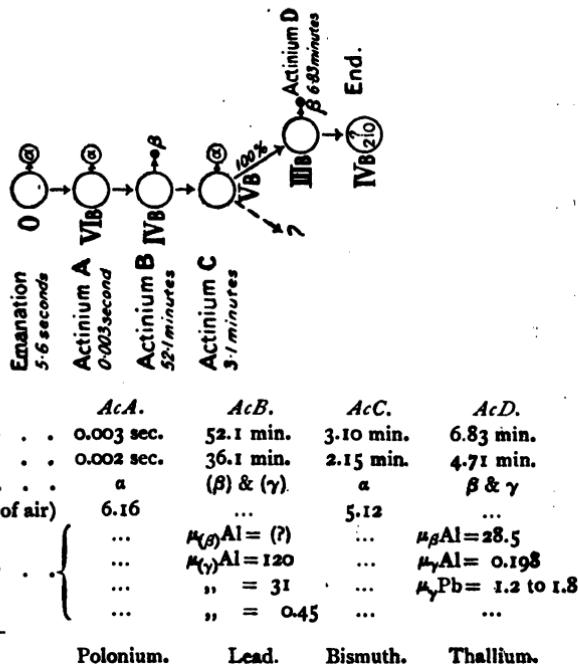
Disintegration product—Actinium A.

The emanation of actinium, except that it has a still shorter period than that of thorium, resembles the other two emanations closely. Actinium preparations generally consist for the most part of hydroxides of the rare earths, which evolve their emanation with great facility, and this and the short period account for the beautiful effects due to the emanation

obtainable from most actinium preparations, as already described under *Actinium*. The diffusion coefficient is 0.11, distinctly greater than that of the other two emanations.¹¹⁴ In still air, of course, the emanation can diffuse only a very short distance from its point of origin before it disintegrates. The emanation is condensed by cold over the range from -100° to -143° .¹¹⁵ So far as is known, it is not chemically absorbed by any reagent, and is therefore presumably a member of the argon family.

More recently it has been found that the change of the actinium emanation is complex. Two sets of α -rays of different ranges are expelled, the α -ray of longer range coming from the product of the emanation. This product has an excessively short period of life, and is attracted to the negative electrode like an active deposit. It has therefore been named Actinium A, and will be considered under the "Active Deposit."

ACTINIUM "ACTIVE DEPOSIT"



The main differences between the active deposit of actinium and that of the other series are, firstly, the shortness of the period of actinium C, which is shorter than that of actinium D, and secondly the fact that what corresponds with the minor branches in the other two series is here, if not the only branch, the only branch the existence of which has been put beyond all doubt. (See Part II., p. 26.)

The actinium active deposit bears the closest analogy to the thorium active deposit, the periods of the B and C members being, however, much shorter, and that of the D member somewhat longer than in the latter case. The period of the active deposit as a whole is very similar to, being rather longer than, that of the radium active deposit after the rapid changes due to the A products are at an end. There is a slight initial lag in the decay of the actinium active deposit as a whole, similar to, but much less pronounced than, that in the case of the thorium active deposit. After this initial lag the decay continues exponentially to zero with the half-period of 36.1 minutes due to actinium B, the longest-lived member of the group.

Actinium A.—The recently discovered first member, actinium A, gives α -rays, and has the shortest period so far actually measured. The period of half-change has been measured accurately by a rotating disc method, and found to be exactly 1/500th of a second.¹⁰² Actinium A may be put into evidence as a distinct product of the emanation by methods similar to those described under *Thorium A*. It is of interest that Giesel,¹¹⁶ so long ago as 1903, working with a powerful emanium preparation, observed that the emanation could be influenced and directed by an electric field. If the preparation was contained in an earthed vessel with an opening of any shape, on bringing a zinc sulphide screen, negatively charged, opposite the opening, a bright image of the latter appeared on the screen as a phosphorescent patch, and disappeared instantly the field was interrupted or screened. He termed the phenomenon the "E-Rays." This experiment is very analogous to that already described under *Thorium A*. In all ordinary work actinium A and the emanation act together as a single product, and their effects are superimposed.

Actinium B.—Actinium B is more volatile than actinium

C, and on heating a wire or plate coated with the active deposit strongly for half a minute the α -activity is not itself volatilised but decays with great rapidity after the heating, with the period of actinium C, the actinium B being almost completely volatilised. The β -activity of the wire or plate after heating, on the contrary, rapidly increases to a maximum and then decays with the somewhat longer period of actinium D. The latter substance is thus volatilised with the actinium B.

Actinium C.—At one time it was thought that actinium C, like thorium C, gave out two sets of α -rays of different, but, in this case, very similar ranges. This, however, has been shown to be unfounded. Among the α -rays of range 5.12 cm., a very small proportion, 0.17 %, has been found with range 6.1 cms., which may be due to a product, AcC' , analogous to that in the other series.¹¹⁷ But this still awaits confirmation.

Actinium D.—Actinium D can also be prepared pure by recoil from the active deposit, the active plate being positively charged and opposed by a similar negatively charged plate, at a short distance, on which the recoiled product is received. The yield may be as much as 50 % of the theoretically possible. Its activity is solely confined to β - and γ -rays, and decays exponentially with the half-period of 5.1 minutes. Actinium D is alone withdrawn from an acid solution of the active deposit by boiling with animal charcoal or platinum black.¹¹⁸ It has been experimentally shown to possess the reactions of thallium in the same way as thorium D.

The decay of the active deposit is complete, and is regular right up to the end, and there is no direct evidence whatever as to the identity or atomic weight of the ultimate product, which, theoretically, should be the isotope of lead.

THE ULTIMATE PRODUCTS—ATOMIC WEIGHT OF LEAD

The remarkable fact emerging from the generalisation, shown in Fig. 3, that all the series end in the same place in the Periodic Table, namely, that occupied by lead, and therefore should be chemically identical with and non-separable from lead, has stimulated investigation of the atomic weight of lead derived from radioactive minerals. The results, so far as they have been obtained, appear favourable to this hypothesis.

As the result of a preliminary examination of the atomic weight of lead derived from Ceylon thorite, a mineral to the unique character of which, as an almost pure thorium mineral, frequent reference has already been made, an atomic weight of 208.4, relative to that of ordinary lead as 207.1, was obtained.¹¹⁹ Assuming that the ultimate products of both the uranium and thorium series are completely stable, and accumulate in geological time, which is the point most in doubt, the 0.4 % of lead present in Ceylon thorite, if entirely of radioactive origin, should consist of about ten parts of "thorium lead" per one part of "uranium lead," and its atomic weight should therefore be about 208.2. The question is being re-examined with a considerably larger quantity of the mineral.

Almost immediately afterwards, careful estimations of the atomic weight of lead from a variety of uranium and thorium minerals by several independent workers were published. In one set the following results were obtained :¹²⁰

<i>Lead from</i>	<i>Atomic Weight.</i>
Uraninite (N. Carolina)	206.40
Pitch-blende (Joachimsthal)	206.57
Carnotite (Colorado)	206.59
Thorianite (Ceylon)	206.82
Pitch-blende (Cornwall)	206.86
Ordinary lead	207.15

Another worker¹²¹ found that the atomic weight from uranium minerals varied from 206.36 to 206.64, and is

distinctly lower than that from galena (207.01), whilst that from monazite is slightly higher (207.08). Lastly, another determination of the atomic weight of lead derived from Joachimsthal pitch-blende gave the value 206.736.¹²²

Bearing in mind the fact that, in very many of these minerals, the probability is against the whole of the lead having been formed in the mineral itself, and much of it may have been present as an original constituent, the results seem to establish definitely the variation of the atomic weight of lead, and are favourable to the view that the isotope derived from thorium has an atomic weight some two units higher than that derived from uranium. The atomic weight of ordinary lead accords with the view that it may be a mixture of the two isotopes in very similar proportions.

POTASSIUM AND RUBIDIUM

A few words in conclusion may be said regarding the radioactivity of these two elements, though it is doubtful at the present time whether we have to do here with cases of atomic disintegration of the type established for the other radio-elements. All potassium salts show a feeble β -activity, about $1/1000$ th part of the β -activity of uranium. The fact that the so-called "potassium cyanide" of commerce is often exceptional is due to these preparations being largely sodium cyanide. The activity appears to be a specific atomic property of potassium, and has not so far been concentrated from it. Of the other alkali metals and their salts, lithium, sodium, and caesium possess no detectable activity. Rubidium, however, possesses a β -activity similar to that of potassium, but distinct from it. The specific activity of the two elements for thick layers of their salts is very similar, but the potassium β -ray is about nine times more penetrating than that of rubidium. Hence the rays come from greater depths in the case of potassium salts, and the activity of rubidium, allowing for the absorption of the radiations of the salt itself, must really be much greater than that of potassium. The potassium β -rays are described as heterogeneous and of varying degrees of penetrating power. The most penetrating are nearly as penetrating as those of uranium X. They are easily deviated by an electric field. On account of their feebleness these supposed cases of radioactivity are difficult to investigate. The alkali metals under the influence of light emit cathode-rays, that is to say, they possess photoelectric sensitiveness. No special examination seems to have been made of the influence of light on the radioactivity of potassium. It is difficult to believe that the atoms of potassium and rubidium are really disintegrating like those of uranium and thorium until products of the disintegration have been isolated or similar further evidence of the process is obtained. Naturally the facts may be explained by

supposing the existence of minute quantities of new elements, not yet separable chemically from potassium and rubidium respectively, as the cause of the phenomena. But of the existence of two new specific types of β -radiation it is not possible to doubt.¹²⁸



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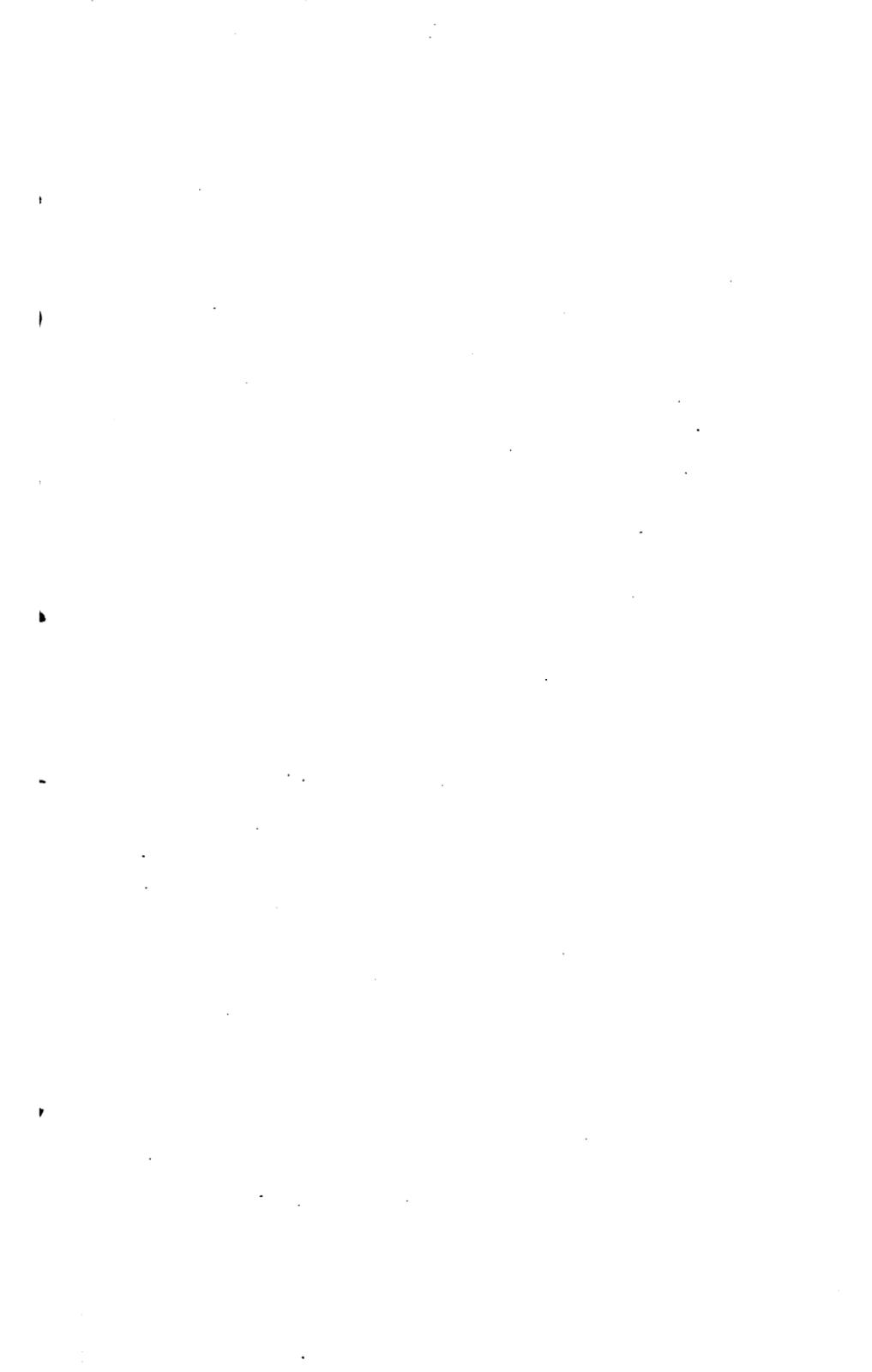
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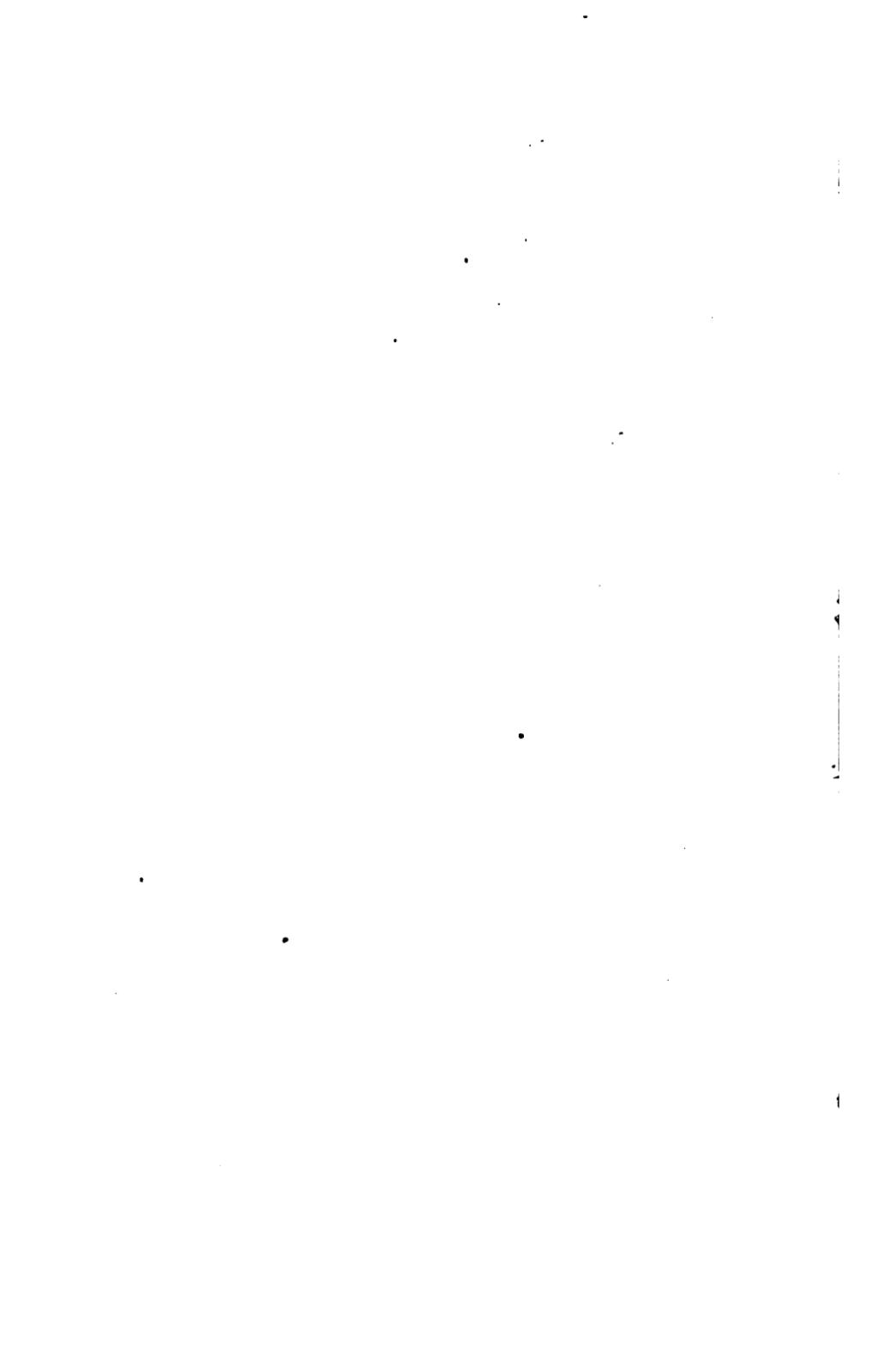
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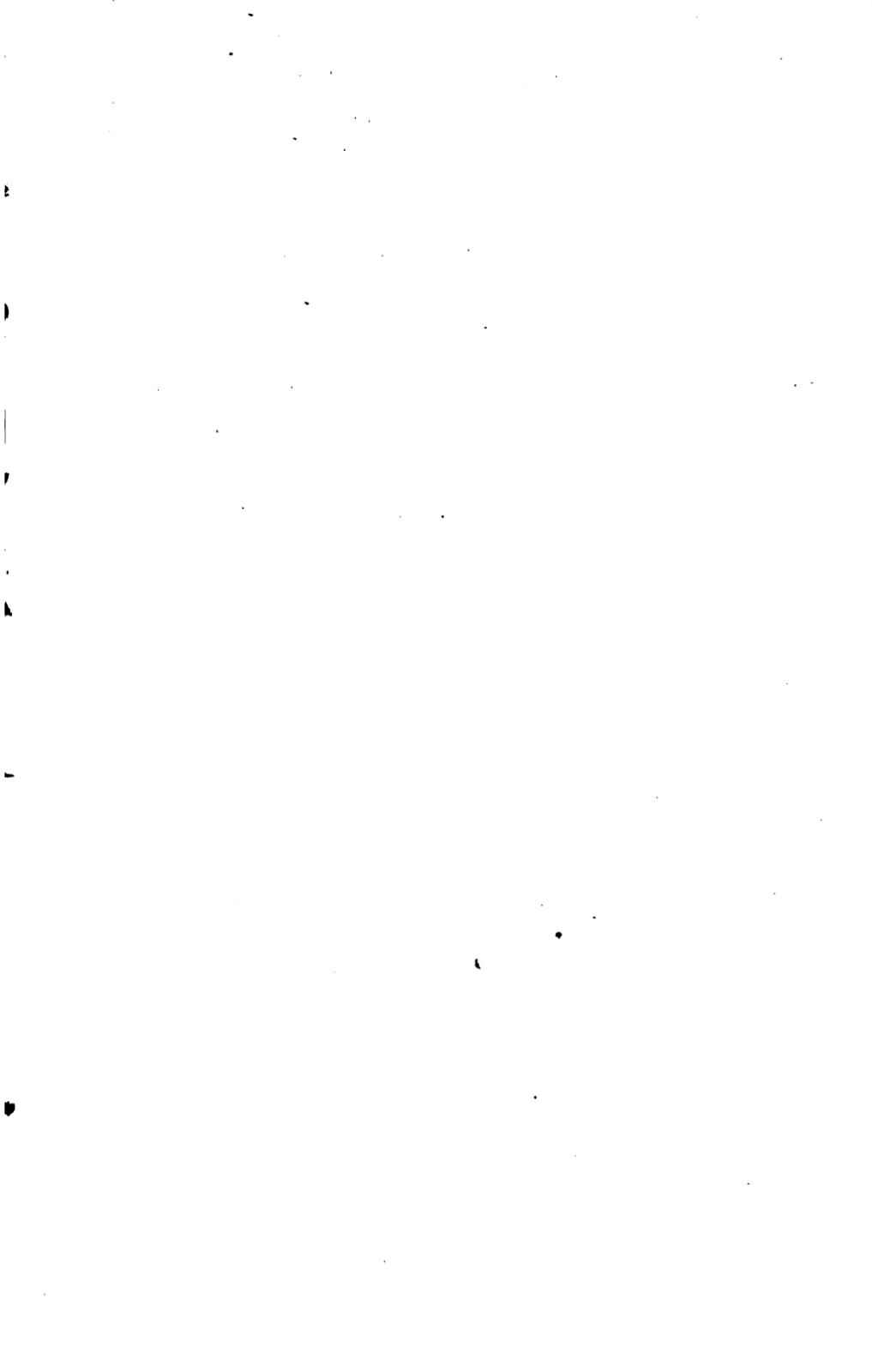
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